374. *Formyl Compounds. Part II.**

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The four *Bz*-formyl-2 : 3-diphenylindoles, three 2 : 3-dimethylindole-aldehydes, and 4-formyldiphenylamine have been prepared and characterised, and the yields of aldehyde obtained by decomposition of 1 : 2 : 3 : 4-tetrahydro-6-toluene-*p*-sulphon- and -6-*p*-nitrobenzenesulphon-hydrazidocarbonylcarbazole and their 9-methyl derivatives with sodium carbonate in glycol and sodium glycollate in glycol have been compared. Azines, acylhydrazones, and one diacylhydrazine have been found as by-products in the McFadyen and Stevens reaction.

The four *Bz*-formyl-2 : 3-diphenylindoles have been prepared by converting the corresponding known acids,[1] into toluene-*p*-sulphonhydrazides which were then heated with sodium carbonate in glycol (McFadyen and Stevens reaction [2]). Three of the four 2 : 3-dimethylindole aldehydes have been similarly prepared. The dimethylindole acids had previously been made by Verkade and Lieste [3] from 1-bromoethyl methyl ketone and the corresponding methyl aminobenzoates: we made them from ethyl methyl ketone carboxyphenylhydrazones by the Fischer reaction. Verkade and Lieste did not prove which was which of the two acids from methyl *m*-aminobenzoate, but from analogy with substituted aminobenzoic acids they suggested that the one with the higher m. p. is the 6-carboxylic acid. Analogy with other indole derivatives supports this view but attempts by Plant and Jones [4] to prove it failed. Efforts to prepare 2 : 3-dimethylindole-4(?)-carbohydrazide were unsuccessful and 4(?)-formyl-2 : 3-dimethylindole has not therefore been made.

The yields obtained were variable (see below), and, as in the carbazole series, were generally better for the hindered positions of the *Bz*-nucleus of the indole. For the 7-, 6-, 5-, and 4-formyldiphenylindole they were 85, 28, 11, and 22% respectively, and for the 7-, 6(?)-, and 5-formyldimethylindoles 60, 4, and 15% respectively.

The new aldehydes resemble those of the carbazole series:[5] common condensations proceed readily but no reactions were found with sodium hydrogen sulphite, Fehling's solution, ammoniacal silver nitrate, potassium cyanide (benzoin-type condensation), or strong alkali (Cannizzaro reaction). Some properties are summarised below:

			Infrared absorption (cm.$^{-1}$) in Nujol paste:	
Indole	M. p.	Colour	CO (stretching)	NH (stretching)
7-Formyl-2 : 3-diphenyl-	137—138° *	Yellow	1665	3330
6- ,, ,, ,,	187—188	Yellow	1660	3240
5- ,, ,, ,,	208—210	Colourless	1670	3300
4- ,, ,, ,,	204—205	Yellow	1655	3250
7- ,, -2 : 3-dimethyl-	126—127	Yellow	1675	3370
(?)6- ,, ,, ,,	95—96	V. pale yellow	1681	3250
5- ,, ,, ,,	137—139	Colourless	1670	3200

* There was evidence for an unstable form, m. p. 121—123°.

Decomposition of 2 : 3-diphenyl-5-toluene-*p*-sulphonhydrazidocarbonylindole produces much azine as well as aldehyde, and 2 : 3-dimethyl-5- and 2 : 3-dimethyl-6(?)-toluene-*p*-sulphonhydrazidocarbonylindole each gave the corresponding formyl-2 : 3-dimethylindole 2′ : 3′-dimethylindolylhydrazone, together with the expected aldehyde.

The formation of by-products in the McFadyen and Stevens aldehyde preparation is of

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* Part I, *J.*, 1957, 2210.

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

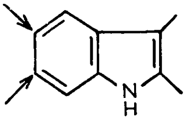
[2] McFadyen and Stevens, *J.*, 1936, 584.

[3] Verkade and Lieste, *Rec. Trav. chim.*, 1946, **65**, 912.

[4] Plant and D. L. Jones, D. L. Jones, Thesis, Oxford, 1956 (unpublished).

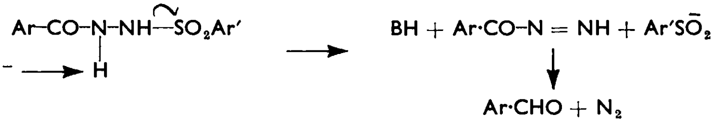
[5] Carter, Plant, and Tomlinson, *J.*, 1957, 2210.

interest. Azines were found as products of decomposition of 1 : 2 : 3 : 4-tetrahydro-6- and 1 : 2 : 3 : 4-tetrahydro-7-toluene-*p*-sulphonhydrazidocarbonylcarbazole and possibly 3-toluene-*p*-sulphonhydrazidocarbonylcarbazole;[5] Dornow and Bormann[6] obtained the acylhydrazone as well as 2-methylnicotinic aldehyde from 3-benzenesulphonhydrazidocarbonyl-2-methylpyridine, and symmetrical diacylhydrazines were obtained from benzenepyrazinoylsulphonhydrazide[7] and 1-benzenesulphonhydrazidocarbonyl-4-nitrobenzene[8] (although the nature of the by-product was not proved in all cases). In the indole series we have found by-products only in positions not adjacent to the ring-junctions * (marked ⟶), which might suggest that steric, rather than electromeric, effects influence their formation or absence. We found, too, that whereas 1-benzenesulphonhydrazidocarbonylnaphthalene gave only 1-naphthaldehyde, yet 2-benzenesulphonhydrazidocarbonylnaphthalene afforded 2-naphthaldehyde together with some *NN'*-di-2-naphthoylhydrazine.

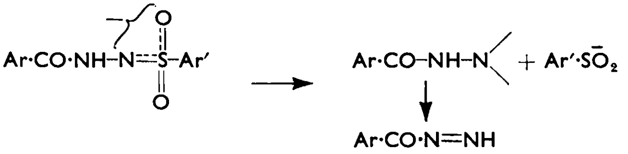


N-Benzoyl-4-toluene-*p*-sulphonhydrazidocarbonyldiphenylamine gives both 4-formyldiphenylamine and its azine. Albert[9] obtained 2-formyldiphenylamine in 80% yield from 2-toluene-*p*-sulphonhydrazidocarbonyldiphenylamine: he does not mention any by-product. The results in the diphenylamine series are therefore similar to those found with indoles and the presence of the NH group may be important. (We have not investigated the preparation of 3-formyldiphenylamine because diphenylamine-3-carboxylic acid has been made only by methods which give very poor yields[10,11] and our attempts to make it by a Chapman rearrangement did not succeed.)

Ingold *et al.*[12] have suggested that the McFadyen and Stevens reaction first involves a bimolecular elimination:



As sodium carbonate converts a sulphonhydrazide into its anion, it seems to us that the initial reaction may be more akin to the begining of the Hofmann degradation of a bromoamide ion in alkali:



Acylhydrazones could then arise by reduction of the $Ar{\cdot}CO{\cdot}N_2H$ fragment, perhaps with sulphinate, followed by condensation with aldehyde, but it seems difficult to explain the formation of azines without recourse to hydrolysis or solvolysis of –CO·NH– bonds: hydrolysis of –NH·SO$_2$– bonds in alkaline media seems unlikely.

In the hope of finding conditions that would produce optimum yields of aldehyde we have compared the amounts of aldehyde obtained when 1 : 2 : 3 : 4-tetrahydro-6-toluene-*p*-sulphon- and -6-*p*-nitrobenzenesulphon-hydrazidocarbonylcarbazole and their 9-methyl

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* This might be further evidence for the view that the acid, m. p. 275—280°, is 6- (and not 4-)carboxy-2 : 3-dimethylindole.

[6] Dornow and Bormann, *Ber.*, 1949, **82**, 216.

[7] Fand and Spoerri, *J. Amer. Chem. Soc.*, 1952, **74**, 1345.

[8] Niemann and Hays, *ibid.*, 1943, **65**, 482.

[9] Albert, *J.*, 1948, 1230.

[10] Gilman, Van Ess, and Shirley, *J. Amer. Chem. Soc.*, 1944, **66**, 1214.

[11] Plant and Worthing, *J.*, 1955, 1278.

[12] Dhar, Hughes, Ingold, Mandour, Maw, and Woolf, *J.*, 1948, 2093.

derivatives were decomposed by sodium carbonate or sodium glycollate in glycol. (These examples were chosen because here we had earlier[5] found particularly poor yields of aldehyde and much azine.) Percentage yields were as follows:

	Toluene-*p*-sulphonhydrazido-derivative with sodium		*p*-Nitrobenzenesulphonhydrazido-derivative with sodium	
	Carbonate	Glycollate	Carbonate	Glycollate
>NH	3·2[5]	30	22	10
>NMe	5·4[5]	34	23	11

Some azine was found in all instances.

4-Formyldiphenylamine is now shown to be a pale yellow solid, m. p. 95—97°; it was earlier described[13] as a brown glass, m. p. about 70°. The *N*-benzoyldiphenylamine-4-carboxylic ester used as starting material was made from *p*-ethoxycarbonylphenyl *N*-phenylbenzimidate by a Chapman rearrangement: the *N*-benzoyl group was lost either during the McFadyen and Stevens reaction or on the alumina during purification of the aldehyde. As stated earlier, similar experiments designed to produce *N*-benzoyldiphenylamine-3-carboxylic esters afforded non-crystalline products. (3-Formyldiphenylamine does not appear to be known: attempts to make both it and its 4-isomer by Chapman rearrangement of the corresponding formylphenyl *N*-phenylbenzimidates were unsuccessful.)

Attempts to make acid chlorides from some of the indole acids mentioned above were successful only in the preparation of 7-chloroformyl-2 : 3-diphenylindole.

EXPERIMENTAL

Ethyl 2 : 3-*Dimethylindole*-7-*carboxylate*.—*Ethyl methyl ketone* o-*carboxyphenylhydrazone* (23 g.) [yellow prisms, m. p. 140° (from methanol) (Found: C, 64·1; H, 6·7. $C_{11}H_{14}O_2N_2$ requires C, 64·1; H, 6·8%)] was boiled (1 hr.) with acetic acid (180 c.c.) and hydrochloric acid (56 c.c.). 2 : 3-Dimethylindole-7-carboxylic acid, m. p. 214—216°, separated from the cooled mixture and was converted into its *ethyl ester*, needles (from ethanol), m. p. 104—106° (Found: C, 71·7; H, 6·9. $C_{13}H_{15}O_2N$ requires C, 71·9; H, 6·7%). Similarly, ethyl methyl ketone *p*-carboxyphenylhydrazone was converted into ethyl 2 : 3-dimethylindole-5-carboxylate, m. p. 110—113°, and *ethyl methyl ketone* m-*carboxyphenylhydrazone* (23 g.) [yellow plates, m. p. 140—141° (from acetic acid) (Found: C, 64·1; H, 7·0%)], boiled with acetic acid (160 c.c.) and hydrochloric acid (50 c.c.), gave, after 30 min., a mixture in which crystals began to appear. Cooling now afforded fairly pure 2 : 3-dimethylindole-6(?)-carboxylic acid (16 g.; m. p. 263—270°); methyl ester, m. p. 175—178° (Verkade and Lieste[3] give m. p. 275—280° and 180—181° for the acid and ester respectively). Dilution of the acetic–hydrochloric acid liquor gave a solid which was extracted with aqueous sodium carbonate to separate the required acid from 2 : 3-dimethylindole. The alkaline extract, on acidification, gave 2 : 3-dimethylindole-4(?)-carboxylic acid (5·5 g.; m. p. 173—177°); methyl ester, m. p. 61—63° (Verkade and Lieste give m. p. 189—190° and 64—65° for the acid and ester, respectively: we did not attempt further purification because the hydrazides are normally more easily purified than are the esters).

2 : 3-*Diphenylindole*-7-*carbohydrazide*.—Methyl 2 : 3-diphenylindole-7-carboxylate was refluxed with hydrazine (100%) for 5 hr. The *hydrazide* formed needles (from ethanol), m. p. 186—187° (Found: C, 76·7; H, 5·0. $C_{21}H_{17}ON_3$ requires C, 77·0; H, 5·2%). Similarly were made: the 6-*carbohydrazide*, plates, m. p. 286—289° (from anisole) (Found: C, 76·7; H, 5·2%); the 5-*carbohydrazide*, needles (from ethanol), m. p. 239° (Found: C, 76·8; H, 5·4%); and the 4-*carbohydrazide*, prisms, m. p. 234° (from ethanol) (Found: C, 76·7; H, 5·0%); also 2 : 3-*dimethylindole*-7-*carbohydrazide*, prisms, m. p. 256—258° (from aqueous acetic acid) (Found: C, 64·7; H, 6·7. $C_{11}H_{13}ON_3$ requires C, 65·0; H, 6·4%); the corresponding 6(?)-*carbohydrazide*, prisms, m. p. 232—235° (from ethanol) (Found: C, 64·8; H, 6·5%); the 5-*carbohydrazide*, m. p. 231—234° (from ethanol) (Found: C, 65·0; H, 6·3%); N-*benzoyldiphenylamine*-4-*carbohydrazide*, m. p. 201—202° (from ethanol) (Found: C, 68·9; H, 5·5. $C_{20}H_{17}O_2N_3,H_2O$ requires

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[13] D.R.P. 103,578.

C, 68·5; H, 5·4%); naphthalene-1-carbohydrazide, needles, m. p. 164—166° (from ethanol) (Stolle and Zinsser[14] give m. p. 166°); naphthalene-2-carbohydrazide, needles, m. p. 147—148° (Pinner[15] gives m. p. 186° and Goldstein and Cornamusaz[16] give m. p. 147·5°). Attempts to prepare 2 : 3-dimethyl-4(?)-carbohydrazide failed: mild conditions left the ester unchanged, more vigorous treatment gave 2 : 3-dimethylindole.

2 : 3-*Diphenyl*-7-*toluene*-p-*sulphonhydrazidocarbonylindole*.—2 : 3-Diphenylindole-7-carbohydrazide (6 g.) and toluene-*p*-sulphonyl chloride (5·8 g.), kept in pyridine solution for 2 hr., afforded, after being poured into dilute hydrochloric acid, 2 : 3-*diphenyl*-7-*toluene*-p-*sulphonhydrazidocarbonylindole* (6·6 g.), needles, m. p. 237° (decomp.) (from acetic acid) (Found: S, 6·8. $C_{28}H_{23}O_3N_3S$ requires S, 6·7%). The following were similarly prepared from the above hydrazides and the appropriate sulphonyl chloride: the 6-*isomer*, prisms, m. p. 250—252° (decomp.) (from ethanol) (Found: C, 70·1; H, 5·0. $C_{28}H_{23}O_3N_3S$ requires C, 69·8; H, 4·8%); the 5-*isomer*, needles, m. p. 249—250° (decomp.) (from ethanol) (Found: C, 69·7; H, 5·0%); and the 4-*isomer*, prisms, m. p. 261° (decomp.) (from ethanol) (Found: C, 69·9; H, 5·0%); also 2 : 3-*dimethyl*-7-*toluene*-p-*sulphonhydrazidocarbonylindole*, prisms, m. p. 232° (decomp.) (Found: C, 60·2; H, 5·2. $C_{18}H_{19}O_3N_3S$ requires C, 60·5; H, 5·3%); 2 : 3-*dimethyl*-6(?)-*toluene*-p-*sulphonhydrazidocarbonylindole*, prisms, m. p. 193° (decomp.) (from aqueous ethanol) (Found: C, 60·4; H, 5·1%); and the 5-*isomer*, prisms, m. p. 245—246° (decomp.) (from ethanol) (Found: C, 60·5; H, 5·3%); 1-*benzenesulphonhydrazidocarbonylnaphthalene*, needles, m. p. 218—219° (decomp.) (from ethanol) (Found: C, 62·7; H, 4·2. $C_{17}H_{14}O_3N_2S$ requires C, 62·6; H, 4·3%); 2-*benzenesulphonhydrazidocarbonylnaphthalene*, needles, m. p. 189° (decomp.) (from ethanol) (Found: C, 62·9; H, 4·3; N, 8·6. $C_{17}H_{14}O_3N_2S$ requires C, 62·6; H, 4·3; N, 8·6%); N-*benzoyl*-4-*toluene*-p-*sulphonhydrazidocarbonyldiphenylamine*, prisms, m. p. 197—198° (decomp.) (from acetic acid) (Found: C, 66·5; H, 4·9. $C_{27}H_{23}O_4N_3S$ requires C, 66·8; H, 4·7%); 1 : 2 : 3 : 4-*tetrahydro*-6-p-*nitrobenzenesulphonhydrazidocarbonylcarbazole*, yellow prisms, m. p. 231—233° (decomp.) (from acetic acid) (Found: C, 54·8; H, 4·3. $C_{19}H_{18}O_5N_4S$ requires C, 55·1; H, 4·3%); and the 9-*methyl homologue*, prisms, m. p. 219—221° (decomp.) (from acetic acid) (Found: C, 55·9; H, 4·6. $C_{20}H_{20}O_5N_4S$ requires C, 56·1; H, 4·7%).

7-*Formyl*-2 : 3-*diphenylindole*.—2 : 3-Diphenyl-7-toluene-*p*-sulphonhydrazidocarbonylindole (18 g.) in dry ethylene glycol (150 c.c.) at 160° was treated with anhydrous sodium carbonate (24 g.) and after 2 min. the mixture was poured into water. The solid was collected, dried, dissolved in benzene, and chromatographed on alumina. 7-*Formyl*-2 : 3-*diphenylindole* (8·5 g.) was obtained as yellow plates, m. p. 138—139°, sintering at 121—123° (from ethanol) (Found: C, 84·6; H, 4·9; N, 4·7. $C_{21}H_{15}ON$ requires C, 84·8; H, 5·0; N, 4·7%). It formed a p-*nitrophenylhydrazone*, red needles, m. p. 240—241° (from acetic acid) (Found: C, 75·0; H, 4·7. $C_{27}H_{20}O_2N_4$ requires C, 75·0; H, 4·6%); a *semicarbazone*, needles, m. p. 209—210° (from ethanol) (Found: C, 74·8; H, 5·2. $C_{22}H_{18}ON_4$ requires C, 74·6; H, 5·1%); and an *anil*, yellow needles, m. p. 157—159° (from ethanol) (Found: C, 86·9; H, 5·6. $C_{27}H_{20}N_2$ requires C, 87·1; H, 5·4%). It condensed with nitromethane (in methanol with sodium hydroxide) to form 7-2′-*nitrovinyl*-2 : 3-*diphenylindole*, red needles, m. p. 197° (from acetic acid) (Found: C, 77·9; H, 4·7. $C_{22}H_{16}O_2N_2$ requires C, 77·6; H, 4·7%); and with malonic acid in pyridine giving 7-2′-*carboxyvinyl*-2 : 3-*diphenylindole*, yellow needles, m. p. 198° (from acetic acid) (Found: C, 81·2; H, 5·2. $C_{23}H_{17}O_2N$ requires C, 81·4; H, 5·0%). The oxime failed to crystallise but gave 7-*cyano*-2 : 3-*diphenylindole* when it was boiled with acetic anhydride (40 min.). This crystallised from benzene as prisms, m. p. 221—223° (Found: C, 85·4; H, 4·9. $C_{21}H_{14}N_2$ requires C, 85·7; H, 4·8%). With dimethylaniline (0·5 g.) and zinc chloride (0·2 g.) at 140—150° for 4 hr. this aldehyde (0·5 g.) gave *bis*-p-*dimethylaminophenyl*-2 : 3-*diphenylindol*-7-*ylmethane*, which crystallised from ethanol as plates, m. p. 189—190° (Found: C, 85·0; H, 6·7. $C_{37}H_{35}N_3$ requires C, 85·2; H, 6·7%). Oxidation with lead dioxide gave a blue-green dye. 7-Formyl-2 : 3-diphenylindole failed to acetylate and its solution in concentrated sulphuric acid was brownish-green.

6-*Formyl*-2 : 3-*diphenylindole*.—The corresponding sulphonhydrazide (8·5 g.) afforded, on decomposition as above, 6-*formyl*-2 : 3-*diphenylindole* (1·5 g.), yellow needles, m. p. 187—188° (from benzene) (Found: C, 85·0; H, 5·2; N, 4·5. $C_{21}H_{15}ON$ requires C, 84·5; H, 5·0; N, 4·7%). It gave a 2 : 4-*dinitrophenylhydrazone*, red prisms, m. p. 304—307° (decomp.) (Found:

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[14] Stolle and Zinsser, *J. prakt. Chem.*, 1906, **74**, 19.
[15] Pinner, *Annalen*, 1897, **298**, 37.
[16] Goldstein and Cornamusaz, *Helv. Chim. Acta*, 1932, **15**, 939.

C, 68·2; H, 3·9. $C_{27}H_{19}O_4N_5$ requires C, 67·9; H, 4·0%); an *azine*, yellow-orange needles, m. p. 280—282° (Found: N, 9·5. $C_{42}H_{30}N_4$ requires N, 9·5%); and an *anil*, yellow prisms, m. p. 199—200° (from ethanol) (Found: N, 7·2. $C_{27}H_{20}N_2$ requires N, 7·5%). From it also were prepared 6-2′-*benzoylvinyl*-2 : 3-*diphenylindole*, orange needles, m. p. 242—243° (from ethanol) (Found: C, 86·6; H, 5·4; N, 3·5. $C_{29}H_{21}ON$ requires C, 87·2; H, 5·3; N, 3·5%), by condensation with acetophenone in alcoholic sodium hydroxide solution, and 6-2′-*acetylvinyl*-2 : 3-*diphenylindole*, orange needles, m. p. 210—212° (from ethanol) (Found: C, 85·4; H, 5·6. $C_{24}H_{19}ON$ requires C, 86·4; H, 5·7%), by interaction with acetone and sodium hydroxide.

5-*Formyl*-2 : 3-*diphenylindole*.—The corresponding sulphonhydrazide (20 g.), decomposed as above, afforded 5-*formyl*-2 : 3-*diphenylindole* (1·4 g.), prisms, m. p. 208—210° (from benzene) (Found: C, 84·8; H, 5·1; N, 4·9. $C_{21}H_{15}ON$ requires C, 84·8; H, 5·0; N, 4·7%). Solid (2·2 g.), insoluble in benzene, was recrystallised from anisole and yielded the *azine* of this aldehyde, prisms, m. p. 329—330°, not depressed by admixture with a specimen made from the aldehyde and hydrazine in ethanol (Found: C, 85·3; H, 5·0; N, 9·2. $C_{42}H_{30}N_4$ requires C, 85·4; H, 5·1; N, 9·5%). This aldehyde gave a 2 : 4-*dinitrophenylhydrazone*, red prisms, m. p. 305—306° (decomp.) (Found: C, 68·0; H, 4·2. $C_{27}H_{19}O_4N_5$ requires C, 67·9; H, 4·0%); a p-*nitrophenylhydrazone*, orange prisms, m. p. 252—254° (from aqueous ethanol) (Found: C, 74·9; H, 4·9. $C_{27}H_{20}O_2N_4$ requires C, 75·0; H, 4·6%); a *semicarbazone*, prisms, m. p. 332—335° (from anisole) (Found: C, 74·2; H, 5·1. $C_{22}H_{18}ON_4$ requires C, 74·6; H, 5·1%); and an *anil*, prisms, m. p. 185—186° (from ethanol) (Found: C, 86·9; H, 5·4. $C_{27}H_{20}N_2$ requires C, 87·1; H, 5·4%). From it was made 5-2′-*acetylvinyl*-2 : 3-*diphenylindole*, yellow prisms, m. p. 240—241° (from ethanol) (Found: C, 85·1; H, 5·8. $C_{24}H_{19}ON$ requires C, 85·4; H, 5·7%). It dissolved in sulphuric acid to form a brick-red solution, it could not be acetylated or methylated, and condensation products with nitromethane and malonic acid did not crystallise.

4-*Formyl*-2 : 3-*diphenylindole*.—The corresponding sulphonhydrazide (3·7 g.) gave 4-*formyl*-2 : 3-*diphenylindole* (0·5 g.), yellow prisms, m. p. 204—205° (from benzene) (Found: C, 85·1; H, 5·2; N, 4·4. $C_{21}H_{15}ON$ requires C, 84·8; H, 5·0; N, 4·7%). It formed a 2 : 4-*dinitrophenylhydrazone*, red prisms, m. p. 310—312° (decomp.) (Found: C, 67·7; H, 4·0. $C_{27}H_{19}O_4N_5$ requires C, 67·9; H, 4·0%); and an *azine*, yellow prisms, m. p. 310—312° (Found: N, 9·0. $C_{42}H_{30}N_4$ requires N, 9·5%).

7-*Formyl*-2 : 3-*dimethylindole*.—The sulphonhydrazide (8·5 g.) gave 7-*formyl*-2 : 3-*dimethylindole* (2·5 g.), yellow needles, m. p. 126—127° (from ethanol) (Found: C, 76·4; H, 6·2; N, 7·8. $C_{11}H_{11}ON$ requires C, 76·3; H, 6·3; N, 8·1%). It formed a 2 : 4-*dinitrophenylhydrazone*, red prisms, m. p. 279—281° (decomp.) (Found: C, 57·4; H, 4·5. $C_{17}H_{15}O_4N_5$ requires C, 57·5; H, 4·2%); a p-*nitrophenylhydrazone*, red prisms, m. p. 212—213° (from ethanol) (Found: C, 66·5; H, 5·4. $C_{17}H_{16}O_2N_4$ requires C, 66·2; H, 5·2%); a *semicarbazone*, needles, m. p. 220—222° (from ethanol) (Found: C, 62·9; H, 6·1. $C_{12}H_{14}ON_4$ requires C, 62·6; H, 6·1%); an *azine*, yellow prisms, m. p. 269—271° (Found: N, 16·2. $C_{22}H_{22}N_4$ requires N, 16·4%); an *anil*, yellow needles, m. p. 74—75° (from ethanol) (Found: C, 82·1; H, 6·5. $C_{17}H_{16}N_2$ requires C, 82·2; H, 6·4%); and an *oxime*, needles, m. p. 99—100° (from ethanol) (Found: C, 70·3; H, 6·4. $C_{11}H_{12}ON_2$ requires C, 70·2; H, 6·4%). 7-*Cyano*-2 : 3-*dimethylindole*, yellow needles, m. p. 158—160° (from light petroleum, b. p. 60—80°) (Found: C, 77·1; H, 5·7. $C_{11}H_{10}N_2$ requires C, 77·6; H, 5·9%), was made by action of acetic anhydride on the oxime. With acetone this aldehyde gave 7-2′-*acetylvinyl*-2 : 3-*dimethylindole*, yellow prisms, m. p. 182—183° (from ethanol) (Found: C, 78·6; H, 7·3; N, 6·6. $C_{14}H_{15}ON$ requires C, 78·9; H, 7·0; N, 6·6%); with nitromethane 2 : 3-*dimethyl*-7-2′-*nitrovinylindole*, red prisms, m. p. 240—242° (from ethanol) (Found: C, 66·6; H, 5·7. $C_{12}H_{12}O_2N_2$ requires C, 66·7; H, 5·6%) was obtained; and it condensed with malonic acid to give 7-2′-*carboxyvinyl*-2 : 3-*dimethylindole*, brown prisms, m. p. 219—220° (decomp.) (from dilute acetic acid) (Found: C, 72·9; H, 5·9. $C_{13}H_{13}O_2N$ requires C, 72·6; H, 6·0%). It formed a pale yellow solution in sulphuric acid.

6-*Formyl*-2 : 3-*dimethylindole*.—The corresponding sulphonhydrazide (5 g.) afforded 6-*formyl*-2 : 3-*dimethylindole* (0·1 g. approx.), pale yellow prisms, m. p. 95—96° (from benzene) (Found: C, 76·2; H, 6·1; N, 8·2. $C_{11}H_{11}ON$ requires C, 76·3; H, 6·3; N, 8·1%). It formed a 2 : 4-*dinitrophenylhydrazone*, brick-red prisms, m. p. >340° (decomp.) (Found: C, 57·8; H, 4·5. $C_{17}H_{15}O_4N_5$ requires C, 57·8; H, 4·2%). This aldehyde was unstable and difficult to elute and its solutions soon became red. Solid (1·5 g.), obtained with the aldehyde, crystallised from nitrobenzene and afforded 6-*formyl*-2 : 3-*dimethylindole* 2′ : 3′-*dimethylindolyl*-6′-*carbonylhydrazone*, yellow prisms, m. p. 309—313° (Found: C, 73·5; H, 6·3. $C_{22}H_{22}ON_4$ requires C, 73·8; H, 6·1%). This was identical (mixed m. p. and infrared absorption) with a specimen prepared by refluxing equivalent quantities of 6-formyl-2 : 3-dimethylindole and 2 : 3-dimethylindole-6-carbohydrazide in ethanol.

5-*Formyl*-2 : 3-*dimethylindole*.—The sulphonhydrazide (15 g.) gave 5-*formyl*-2 : 3-*dimethylindole* (1·05 g.), prisms, m. p. 137—139° (from benzene) (Found: C, 76·4; H, 6·4; N, 8·1. $C_{11}H_{11}ON$ requires C, 76·3; H, 6·4; N, 8·1%). Solid (2 g.), also produced during the decomposition of the sulphonhydrazide, gave prisms (from nitrobenzene), m. p. 314—317°, of 5-*formyl*-2 : 3-*dimethylindole* 2′ : 3′-*dimethyl*-5′-*indolylcarbonylhydrazone*. This was identical (mixed m. p. and infrared absorption) with a synthesised specimen, m. p. 320—323°, prepared as above (Found: C, 73·7; H, 6·3. $C_{22}H_{22}ON_4$ requires C, 73·8; H, 6·1%). 5-Formyl-2 : 3-dimethylindole gave a 2 : 4-*dinitrophenylhydrazone*, red plates, m. p. 290° (decomp.) (Found: C, 58·1; H, 4·5. $C_{17}H_{15}O_4N_5$ requires C, 57·8; H, 4·2%); an *azine*, yellow prisms, m. p. 333—334° (Found: C, 76·7; H, 6·6; N, 16·2. $C_{22}H_{22}N_4$ requires C, 77·2; H, 6·4; N, 16·4%); and an *anil*, pale yellow plates, m. p. 165—166° (from ethanol) (Found: C, 82·0; H, 6·4; N, 11·4. $C_{17}H_{16}N_2$ requires C, 82·2; H, 6·4; N, 11·3%). With acetone it gave 5-2′-*acetylvinyl*-2 : 3-*dimethylindole*, yellow needles, m. p. 147—148° (from aqueous ethanol) (Found: N, 6·6. $C_{14}H_{15}ON$ requires N, 6·6%).

1-*Formylnaphthalene*.—1-Benzenesulphonhydrazidocarbonylnaphthalene (10 g.) was decomposed in ethylene glycol (100 c.c.) with dry sodium carbonate (6·5 g.) at 160° for 2 min. The solution obtained by pouring this mixture into water was extracted with ether which was then shaken with saturated sodium hydrogen sulphite solution: 1-formylnaphthalene sodium bisulphite compound (7·3 g.; equivalent to a yield of about 90%) was obtained. The aldehyde had b. p. 153/12 mm.

2-*Formylnaphthalene*.—The sulphonhydrazide (7·5 g.) was decomposed as above. The ether extract yielded 2-formylnaphthalene [(3 g.), needles (from aqueous methanol), m. p. 58°], and a small amount of solid, insoluble in ether, was recrystallised (twice) from ethanol, forming prisms, m. p. 238—240°, of *NN*′-di-2-naphthoylhydrazine (Found: C, 77·5; H, 5·1; N, 7·9. Calc. for $C_{22}H_{16}O_2N_2$: C, 77·6; H, 4·7; N, 8·2%). The m. p. was not depressed by admixture with a synthetic specimen, m. p. 242—243° (Goldstein and Cornamusaz [16] give m. p. 241°): the mixed m. p. with formylnaphthalene azine (m. p. 232°) was depressed. 2-Formylnaphthalene forms a *hydrazone*, prisms, m. p. 149—151° (from ethanol) (Found: C, 78·2; H, 6·1; N, 16·2. $C_{11}H_{10}N_2$ requires C, 77·6; H, 5·9; N, 16·5%).

† 4-*Formyldiphenylamine*.—(i) *N*-Benzoyl-4-toluene-*p*-sulphonhydrazidocarbonyldiphenylamine (5 g.) in ethylene glycol (20 c.c.) was decomposed with sodium carbonate (12 g.) (2 min. at 160°). The solution was diluted and extracted with benzene, and chromatography of the benzene extract on alumina gave 4-*formyldiphenylamine* (0·65 g.), light yellow needles, m. p. 95—97° (from benzene) (Found: C, 79·0; H, 5·8. $C_{13}H_{11}ON$ requires C, 79·2; H, 5·6%). 4-*Formyldiphenylamine azine* (about 0·2 g.) was obtained partly as a precipitate and partly from the final runnings of the column. It separated from alcohol as yellow plates, m. p. 231—233°, identical (mixed m. p. and infrared absorption) with a synthetic specimen (Found: C, 79·8; H, 5·7. $C_{26}H_{22}N_4$ requires C, 80·0; H, 5·6%). (ii) Decomposition of the above sulphonhydrazide (5 g.) in glycol (20 c.c.) at 160° by adding sodium (1 g.) in glycol (20 c.c.), also at 160°, and dilution with water after 2 min. afforded 4-formyldiphenylamine (0·95 g.) and azine (about 0·2 g.). 4-*Formyldiphenylamine* 2 : 4-*dinitrophenylhydrazone* forms red prisms, m. p. 243—245° (from acetic acid) (Found: C, 60·5; H, 4·2. $C_{19}H_{15}O_4N_5$ requires C, 60·5; H, 4·0%); and the *semicarbazone* forms plates, m. p. 220—223° (from ethanol) (Found: C, 66·1; H, 5·7. $C_{14}H_{14}ON_4$ requires C, 66·1; H, 5·7%).

6-*Formyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*.—(*a*) The toluene-*p*-sulphonhydrazide (4 g.) in ethylene glycol (25 c.c.) was treated at 160° with sodium (2 g.) in glycol (25 c.c.) at 160°. The solution was diluted after 2 min. and worked up as usual, yielding the aldehyde (0·65 g.), m. p. 142—144°. (*b*) Decomposition of 1 : 2 : 3 : 4-tetrahydro-6-*p*-nitrobenzenesulphonhydrazidocarbonylcarbazole (3 g.) in glycol (20 c.c.) with sodium carbonate (6 g.) for 2 min. at 160° gave aldehyde (0·15 g.), m. p. 142—144°. (*c*) Decomposition of the *p*-nitrobenzenesulphonhydrazide (3 g.) as under (*a*) above gave aldehyde (0·31 g.), m. p. 142—144°. Azine (about 0·5 g.) was obtained in each case.

6-*Formyl*-1 : 2 : 3 : 4-*tetrahydro*-9-*methylcarbazole*.—(*d*) Decomposition of the corresponding *p*-toluenesulphonhydrazide (5 g.) as in (*c*) above gave 6-formyltetrahydro-9-methylcarbazole (0·97 g.), m. p. 94—95°. (*e*) Decomposition of the *p*-nitrobenzenesulphonhydrazide (3 g.) as under (*b*) gave aldehyde (0·16 g.), m. p. 94—95°. (*f*) Decomposition of the *p*-nitrosulphonhydrazide (3 g.) as under (*a*) above gave aldehyde (0·34 g.), m. p. 94—95°. Again azine was isolated in each case.

† p-*Ethoxycarbonylphenyl* N-*Phenylbenzimidate*.—Benzanilide (85·6 g.; dried at 100° for 5 hr.) was suspended in dry toluene (400 c.c.) and treated with phosphorus pentachloride (89 g.). After being heated at 100° until evolution of hydrogen chloride ceased (1 hr.), the solution formed was evaporated under reduced pressure. The *N*-phenylbenzimidoyl chloride, which solidified, was dissolved in dry ether (320 c.c.) and filtered slowly into a solution of ethyl *p*-hydroxybenzoate (78·6 g.) in ethanol (320 c.c.) in which sodium (16 g.) had been previously dissolved. The mixture was well stoppered: sodium chloride separated. The solvents were removed by distillation next day; the resulting oil was washed with water; it solidified to give p-*ethoxycarbonylphenyl* N-*phenylbenzimidate*, prisms (from ethanol), m. p. 83—85° (Found: C, 76·6; H, 5·5. $C_{22}H_{19}O_3N$ requires C, 76·6; H, 5·5%). The corresponding p-*methoxycarbonyl-compound*, made by using methyl *p*-hydroxybenzoate in methanol, crystallised in the original reaction mixture, and recrystallised from methanol as prisms, m. p. 107° (Found: C, 76·1; H, 5·3. $C_{21}H_{17}O_3N$ requires C, 76·1; H, 5·1%).

† N-*Benzoyl*-4-*methoxycarbonyldiphenylamine*.—After the above methyl ester (9 g.) had been heated at 270—280° for 2 hr. it cooled to form a glass which crystallised in contact with methanol, from which it was then recrystallised. N-*Benzoyl*-4-*methoxycarbonyldiphenylamine* (7·3 g.) was obtained as prisms, m. p. 107—108°, depressed to 90° by admixture with the starting material (Found: C, 76·1; H, 5·2. $C_{21}H_{17}O_3N$ requires C, 76·1; H, 5·1%). The corresponding *ethoxycarbonyl compound* separated from ethanol as prisms, m. p. 99—101° (Found: C, 76·5; H, 5·7. $C_{22}H_{19}O_3N$ requires C, 76·6; H, 5·5%).

† m-*Carboxyphenyl* N-*Phenylbenzimidate*.—Methyl *m*-hydroxybenzoate was condensed with *N*-phenylbenzimidoyl chloride (as above) but the product did not crystallise. Agitation with aqueous alcoholic potash for 3 hr. at room temperature gave a solution from which acid precipitated m-*carboxyphenyl* N-*phenylbenzimidate*, needles (from ethanol), m. p. 174° (Found: C, 75·6; H, 4·9. $C_{20}H_{15}O_3N$ requires C, 75·7; H, 4·7%). Both this acid and the non-crystalline ester were heated at temperatures between 200° and 300° but the desired diphenylamine was not obtained.

† p-*Formylphenyl* N-*phenylbenzimidate*.—This was prepared as above from benzanilide (24·6 g.) and *p*-hydroxybenzaldehyde (15·3 g.). The product crystallised after prolonged contact with alcohol, from which p-*formylphenyl* N-*phenylbenzimidate* (13·2 g.), prisms, m. p. 73° (Found: C, 79·7; H, 5·0. $C_{20}H_{15}O_2N$ requires C, 79·7; H, 5·0%), was obtained. In a similar way and in comparable yield m-*formylphenyl* N-*phenylbenzimidate* was obtained as needles, m. p. 84° (from ethanol) (Found: C, 79·7; H, 5·1%). Attempts to convert these substances into *N*-benzoylformyldiphenylamines by heat were unsuccessful. The *p*-formyl compound with aniline at 100° (3 hr.) gave an *anil*, needles, m. p. 118° (from ethanol) (Found: C, 82·8; H, 5·5. $C_{26}H_{20}ON_2$ requires C, 83·0; H, 5·3%), which rearranged at 270° (40 min.) giving N-*benzoyl*-4-*phenyliminoformyldiphenylamine*, prisms, m. p. 142° (from ethanol) (Found: C, 82·9; H, 5·3. $C_{26}H_{20}ON_2$ requires C, 83·0; H, 5·3%), which could not be successfully hydrolysed to give 4-formyldiphenylamine.

7-*Chloroformyl*-2 : 3-*diphenylindole*.—The acid (2·2 g.) with thionyl chloride (8 c.c.) was boiled in dry chloroform (40 c.c.) for 1½ hr. The solution was evaporated and the residue was recrystallised from light petroleum (b. p. 60—80°) from which 7-*chloroformyl*-2 : 3-*dimethylindole* separated as yellow prisms, m. p. 140—141° (Found: C, 75·9; H, 4·4. $C_{21}H_{14}ONCl$ requires C, 76·0; H, 4·2%). It gave an *amide*, prisms, m. p. 186—187° (from benzene) (Found: C, 80·4; H, 5·2. $C_{21}H_{16}ON_2$ requires C, 80·8; H, 5·1%), and an *anilide*, needles, m. p. 148—149° (from benzene) (Found: C, 83·8; H, 5·3. $C_{27}H_{20}ON_2$ requires C, 83·5; H, 5·2%).

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