

424. *Formyl Derivatives of Carbazole and 1 : 2 : 3 : 4-Tetrahydrocarbazole.*

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The four carbazolealdehydes and the four *Bz*-aldehydes of tetrahydrocarbazole * have been prepared and characterised. Some of their properties are described and their infrared spectra have been measured.

REFERENCES to *Bz*-formylindole derivatives are rare. 4-Formylindole¹ has been described and several 9-alkyl-3-formylcarbazoles have been prepared by Buu-Hoï and Hoán² who treated 9-alkylcarbazoles with *N*-methylformanilide and phosphorus oxychloride. We therefore decided to investigate the aldehydes of carbazole and tetrahydrocarbazole.

*cyclo*Hexanone *o*-, *p*-, and *m*-carboxyphenylhydrazones readily afford 5 : 6 : 7 : 8-tetrahydrocarbazole-1-, tetrahydrocarbazole-3-, and a mixture of tetrahydrocarbazole-4- and -2-carboxylic acids, respectively: the mixture can be readily separated by fractional crystallisation.^{3,4} These acids formed our obvious starting materials, and we have now shown that their esters can be smoothly dehydrogenated, in quantities up to 5 g., by use

* When not otherwise qualified, tetrahydrocarbazole refers to 1 : 2 : 3 : 4-tetrahydrocarbazole.

¹ Hardegger and Corrodi, *Helv. Chim. Acta*, 1954, **37**, 1826.

² Buu-Hoï and Hoán, *J. Amer. Chem. Soc.*, 1951, **73**, 98.

³ Collar and Plant, *J.*, 1926, 808.

⁴ Moggridge and Plant, *J.*, 1937, 1125.

of palladium-charcoal. The substituent is easily lost if the conditions are too vigorous. We found this method preferable to Barclay and Campbell's chloranil method,⁵ and thus prepared three of the four methyl carbazolecarboxylates (carbazole-4-carboxylic acid itself does not seem to have been described before).

It has not been possible to prepare the corresponding acid chlorides (compare Murphy and Jenkins⁶) except 1-chloroformylcarbazole which was already known⁷ and so we decided to investigate the preparation of the aldehydes by the decomposition of sulphonhydrazides with sodium carbonate in glycol (compare McFadyean and Stevens⁸). It proved possible to make them all by this method. The yields vary considerably and show a correspondence for similar positions of the formyl group in the two series.

1-Formylcarbazole	64%	8-Formyl-1 : 2 : 3 : 4-tetrahydrocarbazole ...	60%
4-Formylcarbazole	67%	5-Formyl-1 : 2 : 3 : 4-tetrahydrocarbazole ...	38.5%
2-Formylcarbazole	34%	7-Formyl-1 : 2 : 3 : 4-tetrahydrocarbazole ...	9.0%
3-Formylcarbazole	7.5%	6-Formyl-1 : 2 : 3 : 4-tetrahydrocarbazole ...	3.2%

Decomposition of 1 : 2 : 3 : 4-tetrahydro-6-, 1 : 2 : 3 : 4-tetrahydro-9-methyl-6-, and 1 : 2 : 3 : 4-tetrahydro-7-(toluene-*p*-sulphonhydrazidocarbonyl)carbazole also affords much of the azine of the expected aldehyde. In addition 3-(toluene-*p*-sulphonhydrazidocarbonyl)carbazole affords some product which seems to be the impure azine. There appears to be no previous reference to the production of azines in this reaction, although Bailey and Staveley⁹ isolated an azine as a by-product in a Huang-Minlon decomposition of a semi-carbazone, which is a related reaction.

The generalisation, that 2- and 3-substituted carbazoles (and corresponding 7- and 6-substituted tetrahydrocarbazoles) have higher melting-points than the 1- and 4-substituted carbazoles (and 8- and 5-substituted tetrahydrocarbazoles), does not hold with the aldehydes. Infrared absorption shows that there is no hydrogen-bonding in 1-formylcarbazole or 8-formyltetrahydrocarbazole. Small variations in the positions of the CO and NH bands are observed, and the CO band in the spectrum of 2-formylcarbazole shows two maxima.

Carbazole	M. p.	Infrared absorption (in Nujol paste).		Colour
		CO stretching, cm. ⁻¹	NH stretching, cm. ⁻¹	
1-Formyl-	143°	1671	3370	Yellow
2- "	155	1670, 1683	3360	V. pale yellow
3- "	153—154	1670	3300	Colourless
4- "	163—164	1679	3200	Yellow
8-Formyltetrahydro-	104	1676	3390	Yellow
7- "	126—128	1667	3300	Yellow
6- "	142—144	1670	3230	Colourless
5- "	144—145	1655	3200	Yellow
6-Formyltetrahydro-9-methyl-	94—95	1671	—	Colourless

These aldehydes are relatively unreactive; they are not readily oxidised by silver nitrate or Fehling's solution, no bisulphite compound has been obtained, and no evidence of a Cannizzaro reaction, "benzoin" condensation, or "mixed benzoin" condensation has been found (although all these reactions have not been attempted with each aldehyde). The common condensation reactions of the formyl group take place normally in most instances. 6-Formyltetrahydrocarbazole is by far the least stable: it is rapidly destroyed in solution. In this it differs from the corresponding 9-methyl compound which suggests that the decomposition is initiated by peroxidation at the 11-position (compare Beer, McGrath, and Robertson¹⁰). The decomposition product does not liberate iodine from acidified potassium iodide solution so that, if a peroxide is involved, it must disappear rapidly.

⁵ Barclay and Campbell, *J.*, 1945, 530.

⁶ Murphy and Jenkins, *J. Amer. Pharm. Assoc.*, 1943, **32**, 83.

⁷ Manske and Kulka, *Canad. J. Res.*, 1950, **28**, B, 443.

⁸ McFadyean and Stevens, *J.*, 1936, 584.

⁹ Bailey and Staveley, *J. Inst. Petroleum*, 1956, 101.

¹⁰ Beer, McGrath, and Robertson, *J.*, 1950, 2118.

When 6-formyl-1:2:3:4-tetrahydrocarbazole azine is heated with palladium-charcoal a colourless compound, $C_{26}H_{20}N_2$, which has an ultraviolet absorption spectrum very similar to that of carbazole, is obtained. This may be 1:2-dicarbazol-3'-ylethane: it cannot be a dicarbazolyethylene.

EXPERIMENTAL

5:6:7:8-Tetrahydrocarbazole-1-carbohydrazide.—Ethyl 5:6:7:8-tetrahydrocarbazole-1-carboxylate (11.5 g.) was refluxed with hydrazine (100%; 90 c.c.) for 5 hr. The hydrazide (11.9 g.) separated as the solution cooled, and formed prisms (from anisole), m. p. 249—251° (Found: C, 67.8; H, 6.7. $C_{13}H_{16}ON_3$ requires C, 68.1; H, 6.5%). The following were also prepared similarly: 5:6:7:8-tetrahydrocarbazole-2-carbohydrazide, needles, m. p. 240—241° (from ethanol) (Found: C, 67.9; H, 6.5%); 5:6:7:8-tetrahydrocarbazole-3-carbohydrazide, prisms, m. p. 200—201° (from aqueous ethanol) (Found: C, 67.9; H, 6.7%); 5:6:7:8-tetrahydrocarbazole-4-carbohydrazide, needles, m. p. 222—224° (from aqueous ethanol) (Found: C, 68.0; H, 6.6%); 5:6:7:8-tetrahydro-9-methylcarbazole-3-carbohydrazide, needles, m. p. 230—233° (from ethanol) (Found: C, 69.4; H, 6.9. $C_{14}H_{17}ON_3$ requires C, 69.1; H, 7.0%); carbazole-1-carbohydrazide, plates, m. p. 250—251° (from ethanol) (Found: C, 69.1; H, 5.0. $C_{13}H_{11}ON_3$ requires C, 69.3; H, 4.9%); carbazole-2-carbohydrazide, prisms, m. p. 276—279° (from acetone) (Found: C, 69.5; H, 5.1%); carbazole-3-carbohydrazide, prisms, m. p. 261—263° (from ethanol) (Found: C, 69.4; H, 5.2%); and carbazole-4-carbohydrazide, needles, m. p. 215—217° (from ethanol) (Found: C, 69.2; H, 5.0%).

1:2:3:4-Tetrahydro-8-(toluene-*p*-sulphonhydrazidocarbonyl)carbazole.—The acid hydrazide (11.5 g.) and toluene-*p*-sulphonyl chloride (11 g.) were kept in pyridine for 2 hr. at room temperature. The mixture was then poured into ice and dilute hydrochloric acid and, when it had been dried, the precipitate was recrystallised from ethanol from which 1:2:3:4-tetrahydro-8-(toluene-*p*-sulphonhydrazidocarbonyl)carbazole (10.5 g.) separated as needles, m. p. 210—212° (decomp.) (Found: C, 62.4; H, 5.7. $C_{26}H_{21}O_3N_3S$ requires C, 62.7; H, 5.5%). The following were obtained similarly: 1:2:3:4-tetrahydro-7-(toluene-*p*-sulphonhydrazidocarbonyl)carbazole, prisms, m. p. 242—243° (decomp.) (from ethanol) (Found: C, 62.7; H, 5.7%); 1:2:3:4-tetrahydro-6-(toluene-*p*-sulphonhydrazidocarbonyl)carbazole, prisms, m. p. 240° (decomp.) (from ethanol) (Found: C, 62.9; H, 5.6%); 1:2:3:4-tetrahydro-5-(toluene-*p*-sulphonhydrazidocarbonyl)carbazole, prisms, m. p. 239—241° (decomp.) (from ethanol) (Found: C, 62.7; H, 5.7%); 1:2:3:4-tetrahydro-9-methyl-6-(toluene-*p*-sulphonhydrazidocarbonyl)carbazole, plates, m. p. 227—228° (decomp.) (from ethanol) (Found: C, 63.4; H, 5.8. $C_{21}H_{23}O_3N_3S$ requires C, 63.5; H, 5.8%); 1-(toluene-*p*-sulphonhydrazidocarbonyl)carbazole, prisms, m. p. 236—237° (decomp.) (from acetic acid) (Found: C, 63.2; H, 4.8. $C_{20}H_{17}O_3N_3S$ requires C, 63.3; H, 4.5%); 2-(toluene-*p*-sulphonhydrazidocarbonyl)carbazole, needles, m. p. 252—255° (decomp.) (from ethanol) (Found: C, 63.4; H, 4.7%); 3-(toluene-*p*-sulphonhydrazidocarbonyl)carbazole, prisms, m. p. 243—245° (decomp.) (from ethanol) (Found: C, 63.3; H, 4.7%); and 4-(toluene-*p*-sulphonhydrazidocarbonyl)carbazole, plates, m. p. 265° (decomp.) (from ethanol) (Found: C, 63.4; H, 4.5%). Yields were comparable, except that the 9-methyl compound was obtained in 88% yield.

8-Formyl-1:2:3:4-tetrahydrocarbazole.—1:2:3:4-Tetrahydro-8-(toluene-*p*-sulphonhydrazidocarbonyl)carbazole (10.2 g.) in ethylene glycol (30 c.c.) was heated in a paraffin-bath to 160° at which temperature anhydrous sodium carbonate (12 g.) was added. Nitrogen was evolved and after 2 min. the mixture was poured into water and extracted with benzene. After it had been dried and concentrated, the benzene layer was passed through activated alumina. The yellow solution from the column afforded 8-formyl-1:2:3:4-tetrahydrocarbazole (3.2 g.; m. p. 98—102°), yellow needles (from ethanol), m. p. 104° (Found: C, 78.3; H, 6.5; N, 7.4. $C_{13}H_{13}ON$ requires C, 78.4; H, 6.5; N, 7.0%). It failed to give a bisulphite compound, and there was no evidence of any change (Cannizzaro reaction) after treatment with 75% potassium hydroxide solution for 75 hr. The aldehyde was recovered in good yield after it had been boiled with alcoholic potassium cyanide solution for 4 hr. When it was similarly treated with benzoin and potassium cyanide there was no sign of the formation of a mixed benzoin. It did not reduce Fehling's solution, or ammoniacal silver nitrate, or colour Schiff's reagent. It proved impossible to obtain an *N*-acetyl compound. With concentrated sulphuric acid it formed a brick-red solution (other tetrahydrocarbazolealdehydes give brown solutions). 8-Formyltetrahydrocarbazole formed a *p*-nitrophenylhydrazone, orange needles, m. p. 235—237° (from acetic

acid) (Found : C, 68.1; H, 5.6. $C_{19}H_{18}O_2N_4$ requires C, 68.2; H, 5.4%); a 2 : 4-dinitrophenylhydrazone, red prisms, m. p. 286° (decomp.) (from anisole) (Found : C, 59.9; H, 4.5. $C_{19}H_{17}O_4N_5$ requires C, 60.1; H, 4.5%); a semicarbazone, needles, m. p. 238—239° (from ethanol) (Found : C, 65.9; H, 6.6. $C_{14}H_{16}ON_4$ requires C, 65.6; H, 6.2%); an azine, yellow prisms, m. p. 286—288° (from ethanol) (Found : N, 14.2. $C_{26}H_{26}N_4$ requires N, 14.2%); and an anil, yellow needles, m. p. 68° (from ethanol), by heating with aniline for 2 hr. (Found : C, 82.9; H, 6.5. $C_{19}H_{16}N_2$ requires C, 83.2; H, 6.6%). Bromination (1 mol.) of 8-formyltetrahydrocarbazole in acetic acid solution, followed by precipitation with water, afforded a compound, $C_{13}H_{14}ONBr$, yellow plates (from ethanol), m. p. 134—135° (Found : C, 56.1; H, 5.2; N, 5.0. $C_{13}H_{14}ONBr$ requires C, 55.7; H, 5.0; N, 5.0%).

9-Acetyl-8-cyano-1 : 2 : 3 : 4-tetrahydrocarbazole.—8-Formyltetrahydrocarbazole oxime, prepared in the usual way, failed to crystallise. When it was boiled with acetic anhydride for 1 hr. it afforded 9-acetyl-8-cyano-1 : 2 : 3 : 4-tetrahydrocarbazole, plates, m. p. 169—170° (from benzene) (Found : C, 71.1; H, 5.6. $C_{15}H_{14}O_2N_2$ requires C, 70.8; H, 5.5%).

1 : 2 : 3 : 4-Tetrahydro-8-2'-nitrovinylcarbazole.—Nitromethane (0.1 g.), 8-formyltetrahydrocarbazole (0.3 g.), and methanol (20 c.c.) were treated at 0° with sodium hydroxide (0.1 g.; in a little water). After $\frac{1}{2}$ hr. the mixture was stirred into ice and hydrochloric acid. 1 : 2 : 3 : 4-Tetrahydro-8-2'-nitrovinylcarbazole (0.2 g.) separated and was recrystallised from benzene. It separated as red needles, m. p. 230—233° (Found : C, 69.4; H, 5.9. $C_{14}H_{14}O_2N_2$ requires C, 69.4; H, 5.8%).

8-2'-Acetylvinyl-1 : 2 : 3 : 4-tetrahydrocarbazole.—A mixture of the aldehyde (0.5 g.) and sodium hydroxide (0.06 g., in a little water) in acetone (25 c.c.) gave 8-2'-acetylvinyl-1 : 2 : 3 : 4-tetrahydrocarbazole (0.3 g.), yellow needles (from ethanol), m. p. 207—208° (Found : C, 80.4; H, 7.3. $C_{16}H_{17}ON$ requires C, 80.3; H, 7.1%).

8-2'-Carboxyvinyl-1 : 2 : 3 : 4-tetrahydrocarbazole.—The aldehyde (0.5 g.), malonic acid (0.5 g.), piperidine (6 drops), and pyridine (6 c.c.) were heated on a steam-bath until effervescence ceased (3 hr.). The solid obtained by precipitation with dilute hydrochloric acid gave 8-2'-carboxyvinyl-1 : 2 : 3 : 4-tetrahydrocarbazole (0.3 g.), pale yellow needles (from ethanol), m. p. 223—225° (decomp.) (Found : C, 74.9; H, 6.4. $C_{15}H_{15}O_2N$ requires C, 74.7; H, 6.2%). This acid decolorised alkaline permanganate rapidly and bromine-water slowly. Attempts to esterify it gave a red solid of high m. p.

7-Formyl-1 : 2 : 3 : 4-tetrahydrocarbazole.—The corresponding toluene-*p*-sulphonhydrazide (15 g.) was decomposed in glycol (50 c.c.) at 160° with anhydrous sodium carbonate (15 g.) as above. The solid formed when the mixture was poured into water was collected and dried. It was only partly soluble in benzene, and the benzene extract, which was chromatographed on alumina, afforded 7-formyl-1 : 2 : 3 : 4-tetrahydrocarbazole (0.7 g.), yellow needles (from benzene), m. p. 126—128° (Found : C, 78.1; H, 6.5; N, 7.1%; *M*, 194. $C_{13}H_{13}ON$ requires C, 78.4; H, 6.5; N, 7.0%; *M*, 199). The residue, which had not dissolved in benzene, was recrystallised from anisole and gave 7-formyl-1 : 2 : 3 : 4-tetrahydrocarbazole azine (1 g.), m. p. 315—318°. This was further recrystallised from ethanol and gave yellow prisms, the m. p. of which was not depressed by admixture with a synthetic specimen, m. p. 332°, prepared by refluxing the aldehyde with hydrazine ($\frac{1}{2}$ mol.) in alcohol for $\frac{1}{2}$ hr. (Found : C, 79.3; H, 6.6; N, 14.1. $C_{26}H_{26}N_4$ requires C, 79.2; H, 6.6; N, 14.2%). 7-Formyltetrahydrocarbazole gave a 2 : 4-dinitrophenylhydrazone, dark red prisms, m. p. 289° (decomp.) (from anisole) (Found : C, 60.0; H, 4.4; N, 18.4. $C_{19}H_{17}O_4N_5$ requires C, 60.1; H, 4.5; N, 18.5%) (this was also obtained from the azine by treatment with 2 : 4-dinitrophenylhydrazine in concentrated sulphuric acid); and an oxime, prisms, m. p. 205—207° (from aqueous ethanol) (Found : C, 72.7; H, 6.8; N, 12.7. $C_{13}H_{14}ON_2$ requires C, 72.9; H, 6.5; N, 13.1%). 7-2'-Acetylvinyl-1 : 2 : 3 : 4-tetrahydrocarbazole was prepared with acetone as above. It formed orange plates, m. p. 175° (from ethanol) (Found : C, 80.4; H, 7.1. $C_{16}H_{17}ON$ requires C, 80.3; H, 7.1%).

6-Formyl-1 : 2 : 3 : 4-tetrahydrocarbazole.—The corresponding sulphonhydrazide (12 g.) was decomposed as for the preparation of the 7-formyl compound. The benzene extract (which had to be kept from unnecessary contact with air and was used rapidly) yielded 6-formyl-1 : 2 : 3 : 4-tetrahydrocarbazole (0.2 g.), almost colourless prisms (from benzene), m. p. 142—144° (Found : C, 78.1; H, 6.7; N, 6.8. $C_{13}H_{13}ON$ requires C, 78.4; H, 6.5; N, 7.0%). The solid which did not dissolve in benzene was extracted with alcohol and then recrystallised from anisole giving 6-formyl-1 : 2 : 3 : 4-tetrahydrocarbazole azine, m. p. 324—327°, identical (mixed m. p.) with a synthetic specimen, plates, m. p. 325—328° (Found : C, 79.2; H, 6.7; N, 13.9. $C_{26}H_{26}N_4$ requires

C, 79.2; H, 6.6; N, 14.2%). The total yield of azine was about 2 g. Benzene solutions of 6-formyltetrahydrocarbazole rapidly deposit a gum on exposure to air and the aldehyde is destroyed: it was not possible to prepare the aldehyde from the azine, but both the aldehyde and its azine could be converted into a 2 : 4-dinitrophenylhydrazone, red prisms, m. p. 286—287° (decomp.) (Found: C, 60.1; H, 4.5; N, 18.4. $C_{19}H_{17}O_4N_5$ requires C, 60.1; H, 4.5; N, 18.5%), and an oxime, prisms, m. p. 175—176° (from aqueous ethanol) (Found: C, 72.6; H, 6.5; N, 12.7. $C_{13}H_{14}ON_2$ requires C, 72.9; H, 6.5; N, 13.1%). When this azine was heated with palladised charcoal under carbon dioxide at 330—350°, and the product was sublimed *in vacuo*, a compound, $C_{26}H_{20}N_2$ (which may be 1 : 2-dicarbazol-3'-ylethane), was obtained. It crystallised from aqueous ethanol as plates, m. p. 187—188° (Found: C, 86.1; H, 5.7; N, 7.8. $C_{26}H_{20}N_2$ requires C, 86.7; H, 5.5; N, 7.8%).

5-Formyl-1 : 2 : 3 : 4-tetrahydrocarbazole.—This compound was prepared by decomposing the sulphonhydrazide (3.5 g.) as for the 8-formyl compound. It crystallised from benzene as yellow prisms (0.7 g.), m. p. 144—145° (Found: C, 78.2; H, 6.5; N, 7.1. $C_{13}H_{13}ON$ requires C, 78.4; H, 6.5; N, 7.0%). It yielded a 2 : 4-dinitrophenylhydrazone, red needles, m. p. 274° (decomp.) (from acetic acid), containing solvent (which could be detected with litmus paper above the melt) (Found: C, 58.9; H, 4.5. $C_{19}H_{17}O_4N_5 \cdot \frac{1}{2}C_2H_4O_2$ requires C, 58.7; H, 4.7%). With acetone this aldehyde gave 5-2'-acetylvinyl-1 : 2 : 3 : 4-tetrahydrocarbazole, yellow prisms, m. p. 241—243° (from ethanol) (Found: C, 80.1; H, 7.2. $C_{16}H_{17}ON$ requires C, 80.3; H, 7.1%).

Methyl 5 : 6 : 7 : 8-tetrahydro-9-methylcarbazole-3-carboxylate.—Methyl 5 : 6 : 7 : 8-tetrahydrocarbazole-3-carboxylate (10 g.) in acetone (200 c.c.) with powdered potassium hydroxide (13.5 g.) was boiled under reflux and treated, during 1 hr., with methyl sulphate (13.6 c.c.) in acetone (13.5 c.c.). After a further hour's boiling the solid was precipitated with water. Recrystallisation from methanol afforded methyl 5 : 6 : 7 : 8-tetrahydro-9-methylcarbazole-3-carboxylate (10.2 g.) as prisms, m. p. 157—159° (Found: C, 74.3; H, 7.1. $C_{15}H_{17}O_2N$ requires C, 74.1; H, 7.0%).

6-Formyl-1 : 2 : 3 : 4-tetrahydro-9-methylcarbazole.—Decomposition of the corresponding sulphonhydrazide (12.2 g.) afforded 6-formyl-1 : 2 : 3 : 4-tetrahydro-9-methylcarbazole (0.35 g.; 5.4%), plates [from light petroleum (b. p. 40—60°)], m. p. 94—95° (Found: C, 78.8; H, 7.1; N, 6.8. $C_{14}H_{15}ON$ requires C, 78.8; H, 7.1; N, 6.6%), and the corresponding azine (*ca.* 1 g.), m. p. 278—281°. In this instance the azine dissolved in benzene and was eluted from the alumina after the aldehyde. It was identical with the azine (yellow prisms; m. p. 278—281°) prepared from the aldehyde and recrystallised from anisole (Found: N, 13.4. $C_{28}H_{30}N_4$ requires N, 13.3%). 6-Formyltetrahydro-9-methylcarbazole 2 : 4-dinitrophenylhydrazone crystallised from anisole as red prisms, m. p. 288° (decomp.) (Found: C, 60.7; H, 4.7. $C_{20}H_{19}O_4N_5$ requires C, 61.1; H, 4.9%).

Methyl Carbazole-2-carboxylate.—Methyl 5 : 6 : 7 : 8-tetrahydrocarbazole-2-carboxylate (5 g.) and palladium-charcoal (1.3 g., containing 5% of Pd) were heated at 280° under carbon dioxide until effervescence was no longer vigorous (about 10 min.). The residue was extracted with acetone, and water precipitated methyl carbazole-2-carboxylate (4 g.), plates (from methanol), m. p. 175—177° (Found: C, 74.7; H, 5.0. $C_{14}H_{11}O_2N$ requires C, 74.7; H, 4.9%). Methyl carbazole-3-carboxylate (4.0 g.) was obtained in the same way from the corresponding tetrahydro-compound (5.0 g.), and was obtained as prisms, m. p. 169—171° (from methanol) (Found: C, 74.3; H, 4.9%), as was methyl carbazole-4-carboxylate, needles, m. p. 96—97° [from light petroleum (b. p. 60—80°)] (Found: C, 74.2; H, 4.9%). Hydrolysis of the latter with aqueous methanolic sodium hydroxide (30 min.) gave carbazole-4-carboxylic acid, prisms, m. p. 244—245° (from benzene) (Found: C, 74.2; H, 4.4. $C_{13}H_9O_2N$ requires C, 73.9; H, 4.3%).

1-Formylcarbazole.—Decomposition of the corresponding sulphonhydrazide (5.5 g.) afforded 1-formylcarbazole (1.8 g.), yellow prisms, m. p. 143° (from ethanol) (Found: C, 80.1; H, 4.7; N, 7.4. $C_{13}H_9ON$ requires C, 80.0; H, 4.6; N, 7.2%). It gave a 2 : 4-dinitrophenylhydrazone, red prisms, m. p. 301—303° (decomp.) (from anisole) (Found: C, 61.0; H, 3.7. $C_{19}H_{13}O_4N_5$ requires C, 60.8; H, 3.5%); a semicarbazone, plates, m. p. 315—318° (from anisole) (Found: C, 66.8; H, 5.0. $C_{14}H_{12}ON_4$ requires C, 66.7; H, 4.8%); and an azine, yellow plates, m. p. 325—326° (from anisole) (Found: N, 14.6. $C_{28}H_{18}N_4$ requires N, 14.5%). From it also were prepared 1-2'-acetylvinylcarbazole, yellow prisms, m. p. 188—190° (from ethanol) (Found: N, 5.6. $C_{18}H_{13}ON$ requires N, 6.0%); and 1-2'-carboxyvinylcarbazole, yellow needles, m. p. 249° (decomp.) (from acetic acid) (Found: C, 75.7; H, 4.7. $C_{15}H_{11}O_2N$ requires C, 75.9; H, 4.6%). Its solution in concentrated sulphuric acid was a characteristic cherry-red.

2-Formylcarbazole.—This compound (0.4 g.) was obtained from the sulphonylhydrazide (2 g.). It formed pale yellow needles, m. p. 155° (from benzene) (Found: C, 79.7; H, 4.6; N, 7.5. $C_{13}H_9ON$ requires C, 80.0; H, 4.6; N, 7.2%). It gave a 2:4-dinitrophenylhydrazone, red prisms, m. p. 328° (decomp.) (Found: C, 60.5; H, 3.5. $C_{19}H_{13}O_4N_5$ requires C, 60.8; H, 3.5%), but an attempt to make the azine gave only the *hydrazone*, prisms, m. p. above 340° (Found: C, 74.5; H, 5.3. $C_{13}H_{11}N_3$ requires C, 74.6; H, 5.3%). Both these derivatives are extremely sparingly soluble and separated pure from the reaction mixture. 2-Formylcarbazole gives a brown solution in sulphuric acid.

3-Formylcarbazole.—Decomposition of the sulphonylhydrazide (5.2 g.) gave 3-formylcarbazole (0.2 g.), prisms, m. p. 153–154° (from aqueous ethanol) (Found: C, 79.7; H, 4.8; N, 7.2. $C_{13}H_9ON$ requires C, 80.0; H, 4.6; N, 7.2%), together with a solid (about 1.5 g.), which it was impossible to recrystallise and which is almost certainly the impure azine. The *azine*, prisms, m. p. 356° (Found: N, 14.0. $C_{26}H_{18}N_4$ requires N, 14.5%), and the red 2:4-dinitrophenylhydrazone, prisms, m. p. 326–328° (decomp.) (Found: C, 60.8; H, 3.8. $C_{19}H_{13}O_4N_5$ requires C, 60.8; H, 3.5%), were prepared: both were too insoluble to be recrystallised. With acetone this aldehyde gave 3-2'-acetylvinylcarbazole, yellow needles, m. p. 160–162° (Found: N, 5.9. $C_{16}H_{13}ON$ requires N, 6.0%). 3-Formylcarbazole gives a brownish-red solution in sulphuric acid.

4-Formylcarbazole.—The sulphonylhydrazide (3.2 g.) gave 4-formylcarbazole (1.1 g.), yellow prisms, m. p. 163–164° (from benzene) (Found: C, 80.0; H, 4.8; N, 7.2. $C_{13}H_9ON$ requires C, 80.0; H, 4.6; N, 7.2%). It gave an *anil*, pale yellow needles, m. p. 151° (from ethanol) (Found: C, 84.4; H, 5.4; N, 9.9. $C_{19}H_{14}N_2$ requires C, 84.4; H, 5.2; N, 10.4%): the 2:4-dinitrophenylhydrazone, red prisms, m. p. 300° (decomp.) (Found: C, 60.7; H, 3.4. $C_{19}H_{13}O_4N_5$ requires C, 60.8; H, 3.5%), and the *azine*, yellow prisms, m. p. 305–307° (Found: N, 14.3. $C_{26}H_{18}N_4$ requires N, 14.5%), crystallised as they were prepared, and were not sufficiently soluble to be recrystallised. A solution of 4-formylcarbazole in sulphuric acid is brick-red.

We acknowledge with gratitude a grant made (to P. H. C.) by Messrs. Albright and Wilson, and we thank Dr. F. B. Strauss for measurements of spectra.

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[Received, January 17th, 1957.]