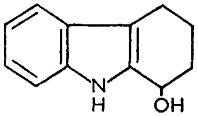
233. *Attempted Synthesis of* 1 : 9-9′ : 1′-*Dicarbazolylene.*

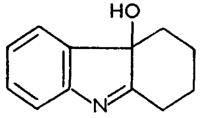
By Ann C. Geale, June M. G. Linnell, and Muriel L. Tomlinson.

The preparations of a number of derivatives of 1 : 9′-dicarbazolyl are described.

The substance $C_{12}H_{13}ON$, obtained from the product of bromination of certain acyltetrahydrocarbazoles[1] and previously thought to be 2 : 3 : 4 : 11-tetrahydro-11-hydroxycarbazole was shown[2] to be 1 : 2 : 3 : 4-tetrahydro-1-hydroxycarbazole (I), and an isomeric compound obtained from bromination of 1 : 2 : 3 : 4-tetrahydroxycarbazole itself,[3] formerly regarded as 1 : 2 : 3 : 10-tetrahydro-10-hydroxycarbazole, was found to be tetrahydro-11-hydroxycarbazolenine (II).[2] Both the compounds (I) and (II), on dehydration, gave a substance originally thought to be 2 : 3-dihydrocarbazole, but as dehydrogenation of the so-called " dihydrocarbazole " afforded a substance $C_{24}H_{14}N_2$, and not carbazole, it became clear that the compound $C_{24}H_{14}N_2$ is 1 : 9-9′ : 1′-dicarbazolylene (IV) and that it had been formed from 1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-octahydro-1 : 9-9′ : 1′-dicarbazolylene (III).[2] It would be desirable to confirm these structures by synthesis of the compounds (III) or (IV) and a number of experiments have been carried out to explore the possibilities of synthesising the latter.

(I)





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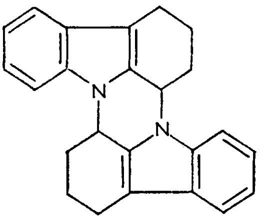

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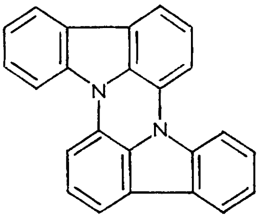

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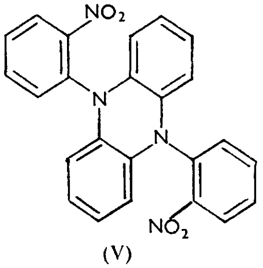

(V)

Wieland and Lecher[4] found that when 4-nitro-*N*-nitrosodiphenylamine was decomposed by boiling it in xylene, 9 : 10-dihydro-9 : 10-di-*p*-nitrophenylphenazine was among the products. It was hoped that, in a similar fashion, 2-nitro-*N*-nitrosodiphenylamine might afford 9 : 10-dihydro-9 : 10-di-*o*-nitrophenylphenazine (V), which could then, perhaps, by reduction and diazotisation, be converted into (IV).

In fact 2-nitro-*N*-nitrosodiphenylamine gave a complex mixture (shown by adsorption on alumina) : the main product was 2 : 4′-dinitrodiphenylamine and the only other crystalline material isolated was some 2-nitrodiphenylamine. (It was later found that Juillard[5] had recorded the production of 2 : 4′-dinitrodiphenylamine by heating this nitrosamine in light petroleum.)

Attention was then turned to the possibility of dehydrogenating 1-9′-carbazolyl-5 : 6 : 7 : 8-tetrahydrocarbazole (VI; R = H), 1 : 9′-dicarbazolyl (VII; R = H), or more highly reduced derivatives of this type. Condensation of 9-*o*-aminophenylcarbazole with

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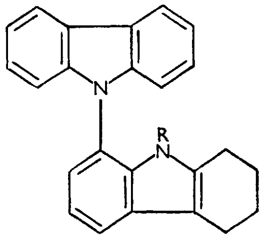
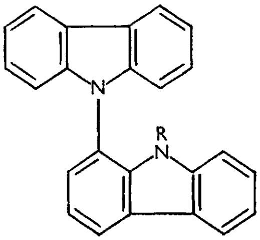
[1] Plant and Tomlinson, *J.*, 1931, 3324.
[2] *Idem, J.*, 1950, 2127.
[3] *Idem, J.*, 1933, 298.
[4] Wieland and Lecher, *Annalen*, 1912, 392, 165.
[5] Juillard, *Bull. Soc. chim.* (*France*), 1905, 33, 1181.

2-hydroxy*cyclo*hexanone proceeded only as far as 9-*o*-(2-oxo*cyclo*hexylamino)phenylcarbazole which could not be cyclised to give the compound (VI; R = H), but this was prepared by the Fischer process from 9-*o*-hydrazinophenylcarbazole and *cyclo*hexanone. It was dehydrogenated smoothly to the desired compound (VII; R = H). Further dehydrogenation, to the dicarbazolylene (IV), could not be brought about by any of the standard methods, such as heating with active palladium catalysts or with sodium aluminium chloride.

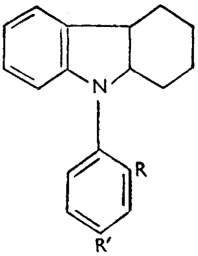
(VI)



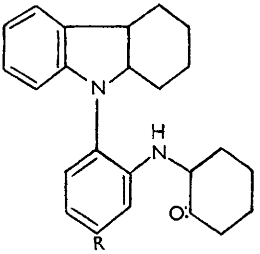


(VII)

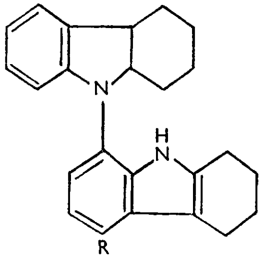
It was, nevertheless, still thought worth while to explore the possibility of cyclising compounds such as (X) during dehydrogenation. It was not possible to condense tetrahydrocarbazole with any *o*-halogenonitrobenzene that was investigated, nor did 1 : 2 : 3 : 4 : 10 : 11-hexahydrocarbazole react with *o*-chloronitrobenzene, but hexahydrocarbazole condensed smoothly with the more reactive 1-chloro-4-cyano-2-nitrobenzene to give 9-(4-cyano-2-nitrophenyl)-1 : 2 : 3 : 4 : 10 : 11-hexahydrocarbazole (VIII; R = NO_2, R′ = CN). The intention was then to convert this into a 9-(1 : 2 : 3 : 4-tetrahydro-8-carbazolyl)-1 : 2 : 3 : 4 : 10 : 11-hexahydrocarbazole (X; R = H or CO_2H or CN) which might ultimately be made into the dicarbazolylene (IV). The compound (VIII; R = NO_2, R′ = CN) was reduced to the amine (VIII; R = NH_2, R′ = CN) and a small quantity of 9-(5-cyano-1 : 2 : 3 : 4-tetrahydro-8-carbazolyl)-1 : 2 : 3 : 4 : 10 : 11-hexahydrocarbazole (X; R = CN) was obtained from this amine and 2-hydroxy*cyclo*hexanone, but the reaction appeared to be capricious and unlikely to yield sufficient material to allow the final cyclisation to be investigated. No greater success was achieved with the acid (VIII; R = NH_2, R′ = CO_2H) obtained by the hydrolysis of the aminonitrile: it could not be converted into a hydrazino-acid, and condensation with 2-hydroxy*cyclo*hexanone proceeded only as far as the formation of 9-(4-carboxy-2-2′-oxo*cyclo*hexylaminophenyl)-1 : 2 : 3 : 4 : 10 : 11-hexahydrocarbazole (IX; R = H) and so this route was abandoned.



(VIII)



(IX)



(X)

1 : 9′-Dicarbazolyl was converted into 9-nitroso-1 : 9′-dicarbazolyl (VII; R = NO) but this did not give the dicarbazolylene (IV) on pyrolysis. Plant and Duthie[6] found that pyrolysis of polycyclic methyl indole-*N*-carboxylates may result in the loss of carbon dioxide to give mixtures of the *N*-methylindole and the indole itself. Various methods were therefore explored in the hope of converting the compounds (VI and VII; R = H)

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[6] Plant and Duthie, *J.*, **1952**, 1899.

into the esters (VI and VII; $R = CO_2Me$) because pyrolysis of these substances might produce the dicarbazolylene (IV), but the hindered NH group failed to react as desired.

EXPERIMENTAL

9-o-*Nitrophenylcarbazole.*—Dunlop and Tucker's method [7] was modified by mixing the carbazole (20 g.), *o*-chloronitrobenzene (40 g.), dry potassium carbonate (20 g.), and copper bronze (0·3 g.) with nitrobenzene (25 c.c.) and refluxing for 5 hr. (yield, 60—65%).

9-o-*Aminophenylcarbazole.*—Reduction of the above nitro-compound, in fine suspension in alcohol, with Adams catalyst and hydrogen at N.T.P. afforded nearly theoretical yields of the pure amine. This method is convenient in small scale work (cf. Dunlop and Tucker [7]).

9-(o-2′-*Oxo*cyclo*hexylaminophenyl*)*carbazole.*—9-*o*-Aminophenylcarbazole (1·3 g.) and 2-hydroxy*cyclo*hexanone (0·55 g.) were heated together at 110—130° until effervescence ceased (20—30 min.). The solid formed crystallised from benzene from which 9-(o-2′-*oxo*cyclo*hexylaminophenyl*)*carbazole* separated as plates, m. p. 156—158° (Found: C, 81·6; H, 6·1. $C_{24}H_{22}ON_2$ requires C, 81·3; H, 6·2%). No further reaction occurred when this substance was heated to 300° with a trace of hydrochloric acid.

9-o-*Hydrazinophenylcarbazole Hydrochloride.*—A fine suspension of the hydrochloride made by warming 9-*o*-aminophenylcarbazole (30 g.) with hydrochloric acid (150 c.c.) and water (30 c.c.) was diazotised at −10° to −5° with sodium nitrite (10 g.) in water (50 c.c.). The deep red diazonium solution was kept at this temperature for ½ hr. and then added, with good stirring, to stannous chloride (65 g.) in hydrochloric acid (100 c.c.) at 0°. The crude hydrazine salt was collected after 4 hr., the colour having changed from red to pale brown. To purify the salt, it was suspended in boiling dilute hydrochloric acid, and hydrogen sulphide was passed in to precipitate the tin. 9-o-*Hydrazinophenylcarbazole hydrochloride* was obtained from the filtrate as plates, m. p. 222—224° (decomp.) (Found: C, 70·0; H, 5·5. $C_{18}H_{15}N_3,HCl$ requires C, 69·8% H, 5·2%).

1-9′-*Carbazolyl*-5 : 6 : 7 : 8-*tetrahydrocarbazole.*—The above pure hydrazine hydrochloride (3 g.), suspended in alcohol (25 c.c.), was treated with ammonia (1·5 c.c.; *d* 0·88) which precipitated the hydrazine as a solid. To this was added *cyclo*hexanone (1 g.) and, after warming and stirring, 9-o-cyclo*hexylidenehydrazinophenylcarbazole* crystallised (3·1 g.). It crystallised from alcohol as needles, m. p. 109—120° (decomp.) (Found: N, 12·2. $C_{24}H_{23}N_3$ requires N, 11·9%). Alternately the crude hydrazine salt (25 g.) in water (500 c.c.) was treated with ammonia until alkaline to litmus. The hydrazine was extracted from the resulting precipitate (which contained tin compounds) with boiling alcohol. Addition of *cyclo*hexanone (10 g.) to this solution afforded the hydrazone which was cyclised to the indole by boiling it (24 g.) with acetic acid (240 c.c.) and hydrochloric acid (110 c.c.) for 20 min. 1-9′-*Carbazolyl*-5 : 6 : 7 : 8-*tetrahydrocarbazole* separated and was collected when cold; it crystallised from aqueous acetic acid (75%) as prisms, m. p. 194—196° (18 g.) (Found: N, 8·3. $C_{24}H_{20}N_2$ requires N, 8·3%). No picrate could be obtained.

1 : 9′-*Dicarbazolyl.*—The above tetrahydro-compound (10 g.) was heated with 10% palladised charcoal at 235—240° in a stream of carbon dioxide for 2 hr. Extraction with boiling alcohol and precipitation with water afforded 1 : 9′-*dicarbazolyl* (7·5 g.). It crystallised from alcohol as plates, m. p. 191°, depressed by admixture with the preceding substance (Found: C, 86·5; H, 4·8; N, 8·6. $C_{24}H_{16}N_2$ requires C, 86·7; H, 4·8; N, 8·4%). Mixed in hot alcoholic solution with picric acid it gave a dark red *picrate* which crystallised from alcohol as prisms, m. p. 140—142° (decomp.) (Found: C, 55·1; H, 2·8. $C_{24}H_{16}N_2,C_6H_3O_7N_3$ requires C, 54·7; H, 2·8%).

9-(4-*Cyano*-2-*nitrophenyl*)-1 : 2 : 3 : 4 : 10 : 11-*hexahydrocarbazole.*—1 : 2 : 3 : 4 : 10 : 11-Hexahydrocarbazole (17·5 g.) and 4-chloro-3-nitrobenzonitrile (18 g.), with anhydrous sodium acetate (10 g.) in alcohol (200 c.c.), were heated on a steam-bath for 10 hr. Red crystals separated and were collected from the cooled solution. After washing with dilute hydrochloric acid they were recrystallised from alcohol from which 9-(4-*cyano*-2-*nitrophenyl*)-1 : 2 : 3 : 4 : 10 : 11-*hexahydrocarbazole* (22 g.) separated as plates, m. p. 170—172° (Found: C, 71·2; H, 5·6. $C_{19}H_{17}O_2N_3$ requires C, 71·5; H, 5·4%).

9-(2-*Amino*-4-*cyanophenyl*)-1 : 2 : 3 : 4 : 10 : 11-*hexahydrocarbazole.*—A mixture of the above nitro-compound (12·8 g.), stannous chloride (46 g.), and glacial acetic acid saturated with hydrogen chloride (150 c.c.) was boiled for ½ hr. The green solution formed was treated with sodium hydroxide (200 g.) in water (1 l.) when it had cooled. The precipitate was collected and extracted with ether from which, after drying and evaporation, a greenish-yellow mass of

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[7] Dunlop and Tucker, *J.*, 1939, 1945.

9-(2-*amino*-4-*cyanophenyl*)-1 : 2 : 3 : 4 : 10 : 11-*hexahydrocarbazole* (10—11 g.) was obtained. After two recrystallisation from alcohol this gave colourless needles, m. p. 176—177° (Found : C, 79·2; H, 6·8. $C_{19}H_{19}N_3$ requires C, 78·9; H, 6·6%).

9-(2-*Amino*-4-*carboxyphenyl*)-1 : 2 : 3 : 4 : 10 : 11-*hexahydrocarbazole*.—The solid which separated after the above amine had been boiled with hydrochloric acid (200 c.c.) for 2 hr. was extracted with sodium carbonate solution and, when this solution was brought to neutrality with dilute acetic acid, the free amino-acid was precipitated. This was dissolved in ether which was then dried and evaporated. The solid 9-(2-*amino*-4-*carboxyphenyl*)-1 : 2 : 3 : 4 : 10 : 11-*hexahydrocarbazole*, so obtained, was recrystallised from benzene from which it separated as needles, m. p. 199° (Found : C, 74·2; H, 6·5. $C_{19}H_{20}O_2N_2$ requires C, 74·0; H, 6·5%). This was converted into 9-(2-*acetamido*-4-*carboxyphenyl*)-1 : 2 : 3 : 4 : 10 : 11-*hexahydrocarbazole* by warming it with a mixture of acetic acid and anhydride. The acetyl compound crystallised from benzene as plates, m. p. 211—214° (Found : C, 72·4; H, 6·5. $C_{21}H_{22}O_3N_2$ requires C, 72·0; H, 6·3%).

9-(4-*Carboxy*-o-2′-*oxo*cyclo*hexylaminophenyl*)-1 : 2 : 3 : 4 : 10 : 11-*hexahydrocarbazole*.—When the above amine (0·5 g.) was heated with 2-hydroxy*cyclo*hexanone (0·2 g.) at 120—140° water was evolved and the solid *product* crystallised from alcohol as needles, m. p. 189—191°, containing alcohol of crystallisation (Found : C, 71·0; H, 7·5; loss at 125° *in vacuo*, 10·4. $C_{25}H_{28}O_3N_2,C_2H_6O$ requires C, 72·0; H, 7·6; C_2H_6O, 10·2%). Reaction appeared to take place at 150—170° when this was heated with a drop of hydrochloric acid, but the product failed to crystallise.

9-(4-*Cyano*-o-2′-*oxo*cyclo*hexylaminophenyl*)-1 : 2 : 3 : 4 : 10 : 11-*hexahydrocarbazole* was prepared from the corresponding cyanide as above. Reaction took place at 120—130° in the presence of a little hydrochloric acid, and the product crystallised from alcohol as needles, m. p. 203—205° (Found : C, 78·0; H, 7·2. $C_{25}H_{27}ON_3$ requires C, 77·9; H, 7·0%). In some experiments when this product was heated to 180—200° with a little hydrochloric acid further loss of water took place and the mass crystallised when rubbed with alcohol. Recrystallisation from acetic acid afforded needles of 9-(5-*cyano*-1 : 2 : 3 : 4-*tetrahydro*-8-*carbazolyl*)-1 : 2 : 3 : 4 : 10 : 11-*hexahydrocarbazole*, m. p. 308—310° (with blackening) (Found : C, 78·3; H, 6·5. $C_{25}H_{25}N_3,\frac{1}{2}C_2H_4O_2$ requires C, 78·6; H, 6·8%). Acetic acid vapour could be detected when the substance was melted.

9-*Nitroso*-1 : 9′-*dicarbazolyl*.—1 : 9′-Dicarbazolyl (1·5 g.) in a little acetic acid was treated with sodium nitrite (0·3 g. in 3 c.c. of water). The yellow precipitate of 9-*nitroso*-1 : 9′-*dicarbazolyl* was collected, washed, and dried. It had m. p. 155° (decomp.) (Found : N, 11·2. $C_{24}H_{15}ON_3$ requires N, 11·6%).

THE DYSON PERRINS LABORATORY, OXFORD.

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