294. *The Fischer Indole Synthesis. Part I.*

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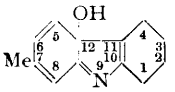
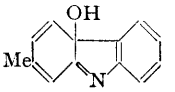
The cyclisation of a number of *o*-substituted phenylhydrazones of *cyclo*hexanone has been studied, and the structure of the by-products (termed 1 : 2 : 3 : 4-tetrahydro*iso*carbazoles) postulated.

In a previous communication (Pausacker and Robinson, *J.*, 1947, 1557) it was noted that two products were produced by the action of dilute sulphuric acid on the 2-chloro-5-methylphenylhydrazone of *cyclo*hexanone. The first product was the expected 8-chloro-5-methyl-1 : 2 : 3 : 4-tetrahydrocarbazole and the other, formed in small yield, was assigned the structure (I). On dehydrogenation, (I) yielded a product which was considered to have structure (II). It is now proposed that these be called respectively 12-hydroxy-7-methyl-1 : 2 : 3 : 4-tetrahydro- and 12-hydroxy-7-methyl-*iso*carbazole.



(I.)



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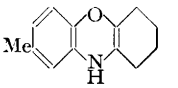

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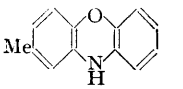


(IV.)

It was suggested that these compounds might possibly have the phenoxazine structures (III and IV) but this was considered unlikely, as their melting points appeared to be too high.

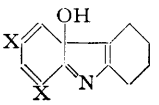
Complete proof that these compounds are not of the phenoxazine type was obtained when 12-*hydroxy*-1 : 2 : 3 : 4-*tetrahydro*iso*carbazole* (V), m. p. 170°, was formed, in small amount, during the cyclisation of the *o*-chlorophenylhydrazone of *cyclo*hexanone by dilute sulphuric acid. Neither the same by-product nor its acetyl derivative was formed when glacial acetic acid was the cyclising agent. It was readily separated from the major product, 8-chloro-1 : 2 : 3 : 4-tetrahydrocarbazole, owing to its sparing solubility in light petroleum (b. p. 40—60°). It was devoid of phenolic properties (*e.g.*, no colour with ferric chloride and insoluble in sodium hydroxide solution) and formed both a *picrate* and an *acetyl* derivative. On dehydrogenation with palladised charcoal, 12-*hydroxy*iso*carbazole* (VI), m. p. 267°, was formed. Phenoxazine has m. p. 156°, so that it is obvious that (VI) cannot be identical with phenoxazine and so the original hypothesis has been confirmed.

Although (V) and (VI) do not display phenolic properties, it is still possible that (V) may be 8-hydroxy-1 : 2 : 3 : 4-tetrahydrocarbazole, formed by hydrolysis of 8-chloro-1 : 2 : 3 : 4-tetrahydrocarbazole, and (VI) may be 1-hydroxycarbazole. This supposes that the phenolic properties are masked in some way by the neighbouring nitrogen atom. Accordingly, 1-hydroxycarbazole (VII) was synthesised as follows. 2-Methoxyphenylhydrazine (Charrier and Casale, *Gazzetta*, 1914, **44**, I, 617; cf. Beilstein, vol. 15, 187) was condensed with *cyclo*hexanone and the corresponding *hydrazone* was cyclised with dilute sulphuric acid. The products formed in this reaction were separated into two fractions by extraction with ether. The ether-insoluble portion was a compound, m. p. 145—146°, assumed to be 12-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*iso*carbazole*, whilst the ether-soluble portion was 8-*methoxy*-1 : 2 : 3 : 4-*tetrahydrocarbazole* (VIII). On dehydrogenation of (VIII) with chloranil (cf. Barclay and Campbell, *J.*, 1945, 530), 1-*methoxycarbazole* (IX) resulted. When palladised charcoal was used as the dehydrogenating agent, a mixture of (IX) and carbazole was formed. On hydrolysis of (IX) with concentrated hydrobromic acid/glacial acetic acid (cf. Stoermer, *Ber.*, 1908, **41**, 323), 1-*hydroxycarbazole* (VII), m. p. 160°, was isolated. It was found to be a typical phenol, dissolving in dilute sodium hydroxide solution and giving a green colour with ferric chloride solution, so it cannot be identical with (VI). A prior claim (D.R.-P. 258,298; Frl., **11**, 170) to the preparation of (VII) has been made, and it was stated to have m. p. 163°. This method of preparation involved the acid hydrolysis of 1-hydroxycarbazole-3 : 6-disulphonic acid at elevated temperature. The latter compound had been prepared by the fusion of carbazole-1 : 3 : 6-trisulphonic acid with sodium hydroxide. As the structure of these sulphonic acids is not known with certainty, it is believed that the above synthesis offers an unambiguous approach to the preparation of (VII).

Similarly, *o*-phenetidine was converted into *o*-ethoxyphenylhydrazine, and on cyclisation with dilute sulphuric acid both 8-*ethoxy*-1 : 2 : 3 : 4-*tetrahydrocarbazole* (X) and 12-*ethoxy*-1 : 2 : 3 : 4-*tetrahydro*iso*carbazole* were isolated. After the dehydrogenation of (X) with bromanil,

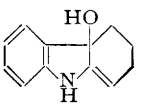
which has been found to be as efficacious as chloranil, 1-*ethoxycarbazole* was formed, which also yielded (VII) upon hydrolysis.

It is now apparent that *o*-halogeno- and *o*-alkoxy-phenylhydrazones of *cyclo*hexanone tend to form both the appropriate tetrahydrocarbazole and tetrahydro*iso*carbazole. Now, if a 2 : 6-substituted phenylhydrazone of *cyclo*hexanone were cyclised, then tetrahydrocarbazole formation would be prevented and tetrahydro*iso*carbazole should be the only product of reaction. This conclusion was verified by examining the cyclisation of the 2 : 4 : 6-trichloro- and 2 : 4 : 6-tribromo-phenylhydrazones of *cyclo*hexanone, whereby (XI) and (XII) respectively were obtained, to which formulæ (XI) and (XII) are assigned. These compounds both formed *picrates* and (XII) also formed an *acetyl* derivative. On dehydrogenation with palladised charcoal in the presence of hydrogen, both compounds were converted into carbazole, thus demonstrating the nature of the fundamental skeleton. Under the same conditions (I) and (V) are simply dehydrogenated to form (II) and (VI) respectively. This difference in reactivity is attributed to the fact that (XI) and (XII) are first dehalogenated, and the hydrogen halide formed then converts the hydroxyl into halogen. Carbazole is then formed by subsequent dehalogenation and dehydrogenation. Furthermore, (XII) was dehydrogenated with bromanil to form 6 : 8-*dibromo*-12-*hydroxy*iso*carbazole* (isolated as its *picrate*).

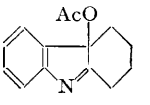


(XI; X = Cl.)

(XII; X = Br.)



(XIII.)



(XIV.)

An attempt is being made to convert either 11-hydroxy-2 : 3 : 4 : 11-tetrahydrocarbazole (XIII) (Plant and Tomlinson, *J.*, 1931, 3330) or 11-acetoxy-1 : 2 : 3 : 4-tetrahydrocarbazolenine (XIV) (Perkin and Plant, *J.*, 1923, **123**, 688) into 12-hydroxy*iso*carbazole (VI).

In many cases the corresponding amine ($Ar{\cdot}NH_2$) has been isolated from the products formed during the cyclisation of the hydrazone $\left(Ar{\cdot}NH{\cdot}N{:}C\begin{<}\begin{matrix}CH_2{-}CH_2\\CH_2{-}CH_2\end{matrix}\end{>}CH_2\right)$.

Further work is proceeding upon the structure of the tetrahydro*iso*carbazoles, and their possible significance in elucidating the mechanism of the Fischer indole synthesis is outlined in the following paper.

Experimental.

(M. p.s are not corrected. Analyses by Drs. Weiler and Strauss, Dr. Tettweiler, and Miss D. Wauchope.)

8-*Methoxy*-1 : 2 : 3 : 4-*tetrahydrocarbazole*.—2-Methoxyphenylhydrazine (Charrier and Casale, *loc. cit.*) was converted into *cyclo*hexanone 2-methoxyphenylhydrazone (XV) in the usual manner. It crystallised from ether as long white needles, m. p. 67—68°, but owing to its instability, it was not analysed. It (68 g.) was added to a mixture of concentrated sulphuric acid (65 ml.) and water (590 ml.) preheated to 90°. After initial reaction, the mixture was heated under reflux (5 minutes). This process is subsequently referred to as " sulphuric acid cyclisation." The resulting mixture was extracted with ether and the ether-insoluble fraction was filtered off and washed with ether. From the combined ethereal extracts, 8-*methoxy*-1 : 2 : 3 : 4-*tetrahydrocarbazole* (XVI) was obtained, b. p. 205—210°/15 mm. (Found : C, 77·3; H, 7·5. $C_{13}H_{15}ON$ requires C, 77·7; H, 7·5%). A very small amount of carbazole (m. p. and mixed m. p. with an authentic specimen, 243°) was also isolated from a high-boiling fraction. *o*-Anisidine (2·8 g.) (identified by its acetyl derivative and picrate) was obtained upon basification of the aqueous portion.

When a concentrated benzene solution of the amorphous ether-insoluble product (11 g.) was allowed to stand in the refrigerator, white crystals (m. p. 137—144°) separated. After crystallisation from light petroleum (b. p. 60—90°), 12-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*iso*carbazole* was obtained as small prisms, m. p. 145—146° (Found : N, 7·0. $C_{13}H_{15}ON$ requires N, 7·0%). It was soluble in concentrated hydrochloric acid, but reprecipitated on addition of water.

Similarly, (XV) (24 g.) was heated under reflux (8 minutes) with glacial acetic acid (250 ml.). The oil precipitated on dilution was immediately extracted with ether and, from the dried ethereal extract, (XVI) (10·4 g.) was again obtained, b. p. 207—210°/14 mm. (Found : C, 77·6; H, 7·3%). *o*-Anisidine (*ca.* 2 g.) was also obtained from the low-boiling fraction.

1-*Methoxycarbazole*.—The compound (XVI) (4·1 g.) was heated under reflux (0·5 hour) with chloranil (10 g.) in sulphur-free xylene (cf. Barclay and Campbell, *loc. cit.*). After filtration, the filtrate was extracted with dilute sodium hydroxide solution, washed with water, and the xylene evaporated under reduced pressure. The residue was dissolved in benzene and chromatographed on an alumina column. That portion of the column giving a blue fluorescence in ultra-violet light was extruded and extracted with acetone; 1-*methoxycarbazole* (XVII) (2·0 g.) was obtained, and crystallised from aqueous ethyl alcohol as long white needles, m. p. 69—70° (Found : C, 79·0; H, 6·0. $C_{13}H_{11}ON$ requires C, 79·1; H, 5·6%). The *picrate* crystallised from aqueous alcohol as orange needles, m. p. 144—145° (Found : C, 53·8; H, 3·4. $C_{19}H_{14}O_8N_4$ requires C, 53·5; H, 3·3%). When (XVI) was dehydrogenated by palladised charcoal in a stream of hydrogen (300°), a mixture of (XVII) and carbazole was obtained.

1-*Hydroxycarbazole*.—1-Methoxycarbazole (0·9 g.) was heated under reflux (2 hours) with glacial acetic acid (10 ml.) and concentrated hydrobromic acid (2 ml.) in an atmosphere of carbon dioxide (cf. Stoermer, *loc. cit.*). The solution was diluted with water, extracted with ether, and the ethereal extract washed, first with sodium hydrogen carbonate solution, and then with water. From the dried ethereal solution, crude 1-*hydroxycarbazole* (XVIII) (0·8 g.) was obtained; it crystallised from water (charcoal) as long white needles, m. p. 160° (Found: C, 79·3; H, 5·3; N, 7·4. $C_{12}H_9ON$ requires C, 78·7; H, 4·95; N, 7·65%). (XVIII) rapidly darkened on exposure to light (cf. 3-hydroxycarbazole), dissolved readily in sodium hydroxide solution, and gave a green colour with ferric chloride solution. When it was dissolved in concentrated sulphuric acid, and a drop of concentrated nitric acid added, a brown colour developed. Carbazole and many of its simple derivatives produced a deep ultramarine-blue colour in this test although exceptions have been noted (Barclay and Campbell, *loc. cit.*). Its *picrate*, which was apparently quite stable, crystallised from water as orange needles, m. p. 191—192° (Found: C, 52·6; H, 3·3. $C_{18}H_{12}O_8N_4$ requires C, 52·4; H, 3·0%). The *acetyl* derivative formed small white prisms, m. p. 132—133°, from water (Found: N, 6·5. $C_{14}H_{11}O_2N$ requires N, 6·7%).

8-*Ethoxy*-1 : 2 : 3 : 4-*tetrahydrocarbazole*.—*o*-Nitrophenetole was prepared from *o*-nitrophenol by van Erp's method (*Ber.*, 1923, **56**, 217) and reduced to *o*-phenetidine by zinc dust and sulphuric acid (cf. Beilstein, Vol. 13, p. 359). *o*-Phenetidine (23 g.) was converted into the corresponding hydrazine by essentially the same method as used by Charrier and Casale (*loc. cit.*) for the preparation of *o*-methoxyphenylhydrazine from *o*-anisidine (cf. also Franzen and Schmidt, *J. pr. Chem.*, 1917, **96**, 17, for the preparation of the hydrazine). The crude hydrazine (18 g.) was then condensed with *cyclo*hexanone, and the resulting hydrazone cyclised with dilute sulphuric acid, the ethereal extract yielding 8-*ethoxy*-1 : 2 : 3 : 4-*tetrahydrocarbazole* (XIX) (10·3 g.), b. p. 180—186°/3 mm. The analysed product had b. p. 172—173°/2 mm. (Found: N, 6·5. $C_{14}H_{17}ON$ requires N, 6·5%). It was later found to crystallise from light petroleum (b. p. 40—60°) as colourless needles, m. p. 75—76°. The *picrate* formed dark red needles from benzene, m. p. 179° (Found: N, 12·5. $C_{20}H_{20}O_8N_4$ requires N, 12·6%). In addition, a tarry product was formed, which was insoluble in both ether and the dilute sulphuric acid. This was dissolved in alcohol, the solution concentrated, and the solid (1·6 g.) formed by the addition of water was centrifuged. After solution in benzene (charcoal), small off-white prisms were formed on evaporation in the air. This compound is assumed to be 12-*ethoxy*-1 : 2 : 3 : 4-*tetrahydro*iso*carbazole*, m. p. 202—204° (from light petroleum, b. p. 100—120°) (Found: N, 6·7. $C_{14}H_{17}ON$ requires N, 6·5%).

1-*Ethoxycarbazole*.—The tetrahydrocarbazole (XIX) (4·3 g.) was heated under reflux (14 hours) with bromanil (17 g.) in sulphur-free xylene (200 ml.). After separation of the tetrabromoquinol, the solution was washed with dilute sodium hydroxide solution and several times with water. After distillation, crude 1-*ethoxycarbazole* (XX) was isolated (3·4 g., b. p. 185—200°/2·4 mm.). Purification through its picrate yielded the pure substance, m. p. 95°, crystallising in white needles from light petroleum (b. p. 60—90°) (Found: N, 6·7. $C_{14}H_{13}ON$ requires N, 6·6%); *picrate* (red needles crystallising from benzene), m. p. 171° (Found: N, 13·1. $C_{20}H_{16}O_8N_4$ requires N, 12·7%). Hydrolysis with hydrobromic acid–acetic acid yielded 1-hydroxycarbazole, identical with the product from the hydrolysis of 1-methoxycarbazole.

12-*Hydroxy*-1 : 2 : 3 : 4-*tetrahydro*iso*carbazole*.—The *o*-chlorophenylhydrazone of *cyclo*hexanone (57 g.) was cyclised with dilute sulphuric acid, and the resulting dark oil extracted with ether. A light purple solid (1·3 g.) was insoluble in both the ether and dilute sulphuric acid. This compound has not been investigated further. Distillation of the ethereal extract gave a fraction (35·2 g., b. p. 160—180°/4 mm.) which deposited a white solid (1·7 g.) upon the addition of light petroleum (b. p. 40—60°). The major product, *i.e.*, the known 8-chloro-1 : 2 : 3 : 4-tetrahydrocarbazole, remained in solution. The solid was 12-*hydroxy*-1 : 2 : 3 : 4-*tetrahydro*iso*carbazole* (XXI), crystallising from light petroleum (b. p. 100—120°) as white needles, m. p. 172° [Found: C, 77·0; H, 6·9; N, 7·3; *M* (Rast), 183. $C_{12}H_{13}ON$ requires C, 77·0; H, 7·0; N, 7·5%; *M*, 187]. A further quantity was obtained from the residue of the above distillation; *picrate* (microscopic dark-red needles crystallising from benzene), m. p. 166° (Found: C, 51·4; H, 3·8; N, 13·4. $C_{18}H_{16}O_8N_4$ requires C, 51·9; H, 3·9; N, 13·4%); *acetyl* derivative (white needles from light petroleum, b. p. 100—120°), m. p. 135—136° (Found: N, 6·2. $C_{14}H_{15}ON$ requires N, 6·1%). The original dilute sulphuric acid solution gave a positive test for chloride ion, and after basification, yielded a small amount of *o*-chloroaniline (identified as acetyl derivative). The substance (XXI) was insoluble in dilute sodium hydroxide solution, gave a negative ferric chloride colour, and its benzene solution showed a strong blue fluorescence in ultraviolet light.

When glacial acetic acid was used as the cyclising agent, 8-chloro-1 : 2 : 3 : 4-tetrahydrocarbazole was again isolated in good yield, but neither (XXI) nor its acetyl derivative could be detected. The only by-product isolated was the *acetyl* derivative of *o*-chlorophenylhydrazine, crystallising from light petroleum (b. p. 100—120°) as white needles, m. p. 119—120° (Found: N, 14·9. $C_8H_9ON_2Cl$ requires N, 15·2%).

Dehydrogenation of (XXI) (0·5 g.) with palladised charcoal (0·2 g., 3 hours at 280—300°) gave 12-*hydroxy*iso*carbazole* (0·3 g.), crystallising from light petroleum (b. p. 100—120°) as white plates, m. p. 267° (Found: N, 7·6. $C_{12}H_9ON$ requires N, 7·7%).

6 : 8-*Dibromo*-12-*hydroxy*-1 : 2 : 3 : 4-*tetrahydro*iso*carbazole*.—*s*-Tribromoaniline was converted into 2 : 4 : 6-tribromophenylhydrazine (Neufeld, *Annalen*, 1888, **248**, 96); the dry hydrazine was heated (2 hours) on the water-bath under reduced pressure with a slight excess of *cyclo*hexanone, and the *hydrazone* (XXII) thus formed crystallised from alcohol as white needles, m. p. 74° (Found: C, 33·6; H, 3·25. $C_{12}H_{13}N_2Br_3$ requires C, 33·9; H, 3·1%).

(*a*) *Cyclisation with dilute sulphuric acid.* The hydrazone (XXII) (71 g.) was heated under reflux (0·5 hour) with sulphuric acid (50 ml. diluted with 450 ml. water). Steam-distillation yielded crude *s*-tribromobenzene (16 g.), crystallising from ethyl alcohol as long white needles, m. p. and mixed m. p. with an authentic specimen 122° (Found: C, 23·2; H, 1·3; Br, 75·7. Calc. for $C_6H_3Br_3$: C, 22·9; H, 1·0; Br, 76·1%). The exact origin of this substance is in doubt although it is known (Chattaway and Irving, *J.*, 1931, 1741) that *s*-trichlorophenylhydrazine is readily oxidised to *s*-trichlorobenzene. The residue was extracted with ether (bromide ion was detected in the aqueous solution) and, after

evaporation, a brown oil (40 g.) remained. This was heated under reflux with benzene, and after concentration (to *ca.* 75 ml.), light petroleum (b. p. 60—90°) was added. The dirty solid (17·3 g.) precipitated was discarded, and the filtrate evaporated to dryness and then dissolved in light petroleum (b. p. 60—90°). After being left overnight in the refrigerator, crystals (6·9 g.) had separated which proved to be identical with *s*-tribromoaniline (m. p. and mixed m. p. with an authentic specimen, 122°). After evaporation of the light petroleum a dark oil (12·3 g.) remained. This was heated with picric acid (8·3 g.) in benzene; 6 : 8-*dibromo*-12-*hydroxy*-1 : 2 : 3 : 4-*tetrahydro*iso*carbazole* (as XII) *picrate* (14 g.) was obtained, m. p. 142—144°, which after crystallisation from light petroleum (b. p. 60—90°) formed orange needles, m. p. 144—145° (Found : N, 10·1. $C_{18}H_{14}O_8N_4Br_2$ requires N, 9·8%). Decomposition of the picrate with dilute sodium hydroxide solution gave the *carbazole* (XII), crystallising from ethyl alcohol as thick rods, m. p. 93—94° (Found : N, 4·2. $C_{12}H_{11}ONBr_2$ requires N, 4·1%). Its *acetyl* derivative was prepared by heating (water-bath) with acetic anhydride containing a trace of concentrated sulphuric acid. It crystallised from methyl alcohol in fine white needles, m. p. 139—140° (Found : N, 3·7. $C_{14}H_{13}O_2NBr_2$ requires N, 3·6%).

After dehydrogenation (4 hours, 300°) of (XII) (0·5 g.) mixed with palladised charcoal (0·15 g.) in a stream of hydrogen, carbazole (0·07 g.) was isolated, m. p. and mixed m. p. with an authentic specimen 243° (Found : N, 8·2. Calc. for $C_{12}H_9N$: N, 8·4%).

The carbazole (XII) (1 g.) was refluxed (41 hours) with bromanil (2·46 g.) in sulphur-free xylene (30 ml.). After separation of the tetrabromoquinol, etc. (see above), a brown oil (0·7 g.) resulted. This was treated with picric acid (0·7 g.) in benzene, and the *picrate* of 6 : 8-*dibromo*-12-*hydroxy*iso*carbazole* was obtained, crystallising from light petroleum (b. p. 100—120°) as orange needles, m. p. 118° (Found : N, 10·3. $C_{18}H_{10}O_8N_4Br_2$ requires N, 9·8%).

(*b*) *Cyclisation with glacial acetic acid.* The hydrazone (XXII) (83 g.) was heated under reflux (0·5 hour) with glacial acetic acid (450 ml.), a dark brown solution being obtained. After separation of the crystals precipitated during the reaction (10 g., found to be ammonium bromide), the solution was concentrated in a vacuum on the water-bath. Distillation of the residue gave the following fractions: (i) <130°/3 mm. (3·2 g.); (ii) 130—190°/0·8 mm. (10·7 g.); (iii) 190—210°/0·8 mm. (11·3 g.). Fraction (i) was found to consist principally of *s*-tribromobenzene, and fraction (ii) to be *s*-tribromoaniline. Fraction (iii), after purification through its picrate, yielded (XII) (6·8 g.), identical with the product formed in method (*a*).

6 : 8-*Dichloro*-12-*hydroxy*-1 : 2 : 3 : 4-*tetrahydro*iso*carbazole*.—2 : 4 : 6-Trichlorophenylhydrazine (prepared according to the method given by Chattaway and Irving, *loc. cit.*) was condensed with *cyclo*hexanone; the phenylhydrazone (XXIII) crystallised from methyl alcohol as white needles, m.p. 72°, which decomposed on standing. It (28 g.) was heated under reflux (1 hour) in glacial acetic acid (200 ml.). The precipitated solid (ammonium chloride) was filtered off, and the glacial acetic acid was removed in a vacuum. On steam-distillation, *s*-trichloroaniline (3·8 g.) was obtained (m. p. and mixed m. p. with an authentic specimen 77°). The residue was extracted with ether and, after distillation, yielded crude 6 : 8-*dichloro*-12-*hydroxy*-1 : 2 : 3 : 4-*tetrahydro*iso*carbazole* (XI) (7·8 g.), b. p. 196—206°/0·6 mm.; on redistillation, b. p. 188—190°/0·3 mm. (Found : N, 6·2. $C_{12}H_{11}ONCl_2$ requires N, 5·5%); the *picrate* formed fine copper-coloured needles [from light petroleum (b. p. 60—90°)], m. p. 114—115° (Found : N, 12·0. $C_{18}H_{14}O_8N_4Cl_2$ requires N, 11·6%).

When the base (1·2 g.) was heated (5·5 hours at 280—300°) with palladised charcoal (0·3 g.) in a stream of hydrogen until the evolution of hydrogen chloride was complete, the product extracted with acetone, and the residue sublimed at 170—180°/0·3 mm., crystallisation from light petroleum (b. p. 100—120°) afforded pure carbazole (m. p. and mixed m. p. with an authentic specimen, 240°).

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