964. *Peroxides of Tetrahydrocarbazole and Related Compounds. Part IV.* Autoxidation of Substituted Tetrahydrocarbazoles.*

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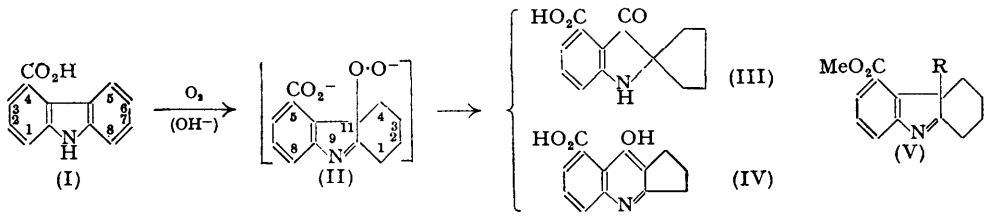
By aeration in alkaline solution 5 : 6 : 7 : 8-tetrahydrocarbazole-4-carboxylic acid (I) is converted into a mixture of 4-hydroxy-2 : 3-*cyclo*pentenoquinoline-5-carboxylic acid (IV) and *cyclo*pentane*spiro*-2-ψ-indoxyl-4-carboxylic acid (III), which are also obtained by the action of alkali on 5-carbomethoxy-1 : 2 : 3 : 4-tetrahydrocarbazol-11-yl hydroperoxide (V; R = O·OH). Alternatively the *spiro*-indoxyl (III) was obtained from the hydroperoxide (V; R = O·OH) by way of the hydroxycarbazolenine (V; R = OH). The results indicate that a peroxide is an unstable intermediate in the autoxidation of the acid (I) in aqueous media.

In autoxidation experiments 5 : 6 : 7 : 8-tetrahydrocarbazole-4-, -3-, -2-, and -1-carboxylic acid show an increasing stability and, similarly, the ease of peroxide formation decreases regularly in the series methyl 5 : 6 : 7 : 8-tetrahydrocarbazole-4-, -3-, -2-, and -1-carboxylate. In general, electron-donating substituents in the benzene ring of tetrahydrocarbazoles facilitate peroxidation, whilst electron-attracting groups have the opposite effect.

The unstable autoxidation product from 1 : 2 : 3 : 4-tetrahydro-6-hydroxycarbazole could not be isolated.

The ready formation of hydroperoxides by certain 1 : 2 : 3 : 4-tetrahydrocarbazoles (Parts I and II, *J.*, 1950, 2118, 3283) suggested that similar processes might be involved in the biological oxidation of indoles, *e.g.*, in the metabolism of tryptophan and the conversion of 5 : 6-dihydroxyindole into melanin. Recent work in this laboratory on melanin formation (to be published elsewhere) now indicates that this type of peroxidation does not play a major part in the oxidative polymerisation, but before this conclusion had been reached we initiated a study on the behaviour of tetrahydrocarbazoles containing solubilising groups—*e.g.*, carboxyl and hydroxyl—which could be subjected to autoxidation in aqueous media. Although previously peroxides have been isolated from tetrahydrocarbazoles in non-polar solvents only, evidence is now presented that they can be formed, as unstable intermediates, in autoxidations occurring in aqueous media.

The effect of aeration on 5 : 6 : 7 : 8-tetrahydrocarbazole-1-, -2-, -3-, and -4-carboxylic acid, dissolved in dilute aqueous sodium hydroxide was studied under standard conditions. Thus the 4-carboxylic acid was slowly converted into a mixture of a colourless, very sparingly soluble, high-melting acid and a yellow fluorescent acid, the isolation of which was difficult. In its characteristic strong green fluorescence in alcoholic solution and in its ultra-violet absorption spectrum, the second acid closely resembled *cyclo*pentane*spiro*-2-ψ-indoxyl (Part I, *loc. cit.*) and is, therefore, formulated as *cyclo*pentane*spiro*-2-ψ-indoxyl-4-carboxylic acid (III).



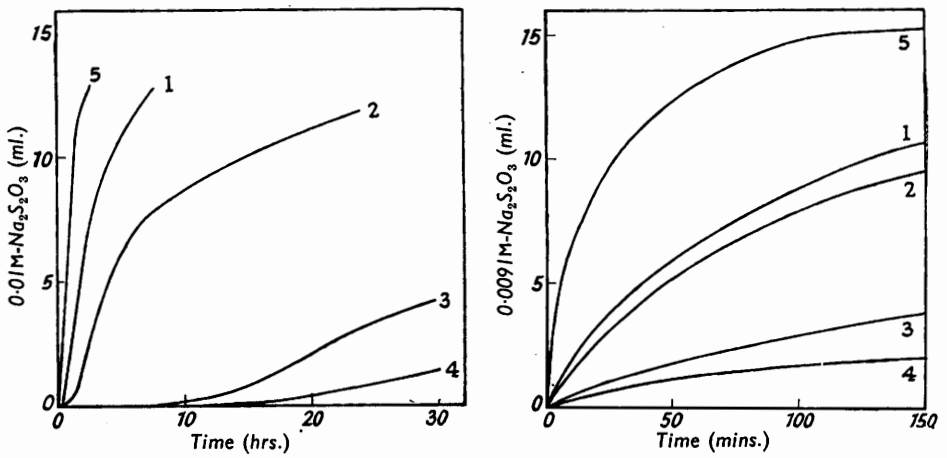
The colourless acid had the expected properties of a carboxy-derivative of 4-hydroxy-2 : 3-*cyclo*pentenoquinoline which is formed together with *cyclo*pentane*spiro*-2-ψ-indoxyl by the action of aqueous sodium hydroxide on 1 : 2 : 3 : 4-tetrahydrocarbazolyl hydroperoxide (Parts I and II, *locc. cit.*) and accordingly, in agreement with the analytical and light-absorption data, it is formulated as 4-hydroxy-2 : 3-*cyclo*pentenoquinoline-5-carboxylic

* Part III, *J.*, 1952, 4351.

acid (IV). By analogy with the behaviour of 1 : 2 : 3 : 4-tetrahydrocarbazolyl hydroperoxide the simultaneous formation of (III) and (IV) from (I) strongly suggests that the autoxidation proceeds by way of an intermediate hydroperoxide or its anion (II) which would be expected to give the observed products.

Under similar conditions the aeration of 5 : 6 : 7 : 8-tetrahydrocarbazole-3- and -2-carboxylic acid gave the corresponding *cyclo*pentenoquinoline-6- and -7-carboxylic acid but the related fluorescent *spiro*-compounds, which were undoubtedly formed, could not be isolated, partly owing to the presence of larger amounts of unchanged starting materials than in the case of (I). On the other hand, 5 : 6 : 7 : 8-tetrahydrocarbazole-1-carboxylic acid was almost completely recovered, although traces of fluorescent material were formed. These results do not provide exact evidence on the relative ease of peroxidation of the four acids in aqueous media but it does appear that the 4-carboxylic acid was most and the 1-carboxylic acid least affected, whilst the 2- and 3-carboxylic acids occupied an intermediate position.

Rates of peroxidation (FIG. 1, *uncatalysed*; FIG. 2, *catalysed by benzoyl peroxide*).



1, 1 : 2 : 3 : 4-*Tetrahydrocarbazole.*
2, *Methyl* 5 : 6 : 7 : 8-*tetrahydrocarbazole-4-carboxylate.*
3, *Methyl* 5 : 6 : 7 : 8-*tetrahydrocarbazole-3-carboxylate.*
4, *Methyl* 5 : 6 : 7 : 8-*tetrahydrocarbazole-2-carboxylate.*
5, 1 : 2 : 3 : 4-*Tetrahydro-6-methoxycarbazole.*

As the tetrahydrocarbazolecarboxylic acids did not undergo peroxidation in organic solvents a study of the relative rates of peroxide formation was not possible. It was found, however, that of the four corresponding methyl esters three formed peroxides in benzene. Thus 5-carbomethoxy-1 : 2 : 3 : 4-tetrahydrocarbazol-11-yl hydroperoxide (V; R = O·OH) was obtained in excellent yield and with cold aqueous sodium hydroxide gave, as expected, mainly (IV) along with a small amount of (III), respectively identical with the products formed by the autoxidation of 5 : 6 : 7 : 8-tetrahydrocarbazole-4-carboxylic acid. A further link between the autoxidation of the acid (I) in aqueous media and the peroxide (V; R = O·OH) was provided by reduction of (V; R = O·OH) with aqueous sodium sulphite to the corresponding hydroxycarbazolenine (V; R = OH) which, by rearrangement with hot methanolic potassium hydroxide, gave the *spiro*-acid (III).

The peroxide of methyl 5 : 6 : 7 : 8-tetrahydrocarbazole-3-carboxylate was obtained in relatively low yield whilst the 2-methyl ester gave a little crude peroxide from which a pure product was not obtained, and the 1-methyl ester did not react.

In order to confirm the remarkable effect suggested by the behaviour of the acids in aqueous solution and of the methyl esters in non-polar solvents, the rate of peroxidation of the esters was studied semiquantitatively by estimating the amount of peroxide iodo-

metrically, the autoxidations being carried out simultaneously under comparable conditions. For comparison 1 : 2 : 3 : 4-tetrahydrocarbazole and 1 : 2 : 3 : 4-tetrahydro-6-methoxycarbazole were included.

The results obtained are illustrated in the Fig. 1. The times for the peroxide titre to rise to one-quarter of the theoretical value ($t_{\frac{1}{4}}$) are tabulated below. Fig. 2 shows the results obtained in the presence of a constant catalytic amount of benzoyl peroxide; even under these conditions peroxide formation by the 1-methyl ester was not observed.

Substance	Unsubs.	4-CO_2Me	3-CO_2Me	2-CO_2Me	1-CO_2Me
$t_{\frac{1}{4}}$ (hr.)	1·7	4·1	38	∞	∞

The gradation in reactivity of the substituted compounds clearly corresponds with that inferred from the qualitative experiments, and the position of attachment of the carboxy- or carbomethoxy-group obviously exerts a subtle influence which does not seem to be capable of any straightforward explanation. Further experiments with other groups of tetrahydrocarbazoles containing a common substituent should at least demonstrate whether the effect is general.

It will be observed that the methyl esters are peroxidised less readily than tetrahydrocarbazole, indicating that the electron-attracting carbomethoxy-group, whatever its position, exerts a deactivating influence. On the other hand, tetrahydro-6-methoxycarbazole, with an electron-donating substituent, is peroxidised appreciably faster than tetrahydrocarbazole. Peroxidation of several other tetrahydrocarbazoles has been studied qualitatively. Thus, 6-bromo- and 6-acetamido-tetrahydrocarbazole readily formed crystalline hydroperoxides, but the 6- and 8-nitro-derivatives were inert. 6-Benzyloxy-1 : 2 : 3 : 4-tetrahydro- and 1 : 2 : 3 : 4-tetrahydro-6-hydroxy-carbazole also resisted peroxidation, but here failure may be due to the chain-breaking action of the substituent groups. It was found, for example, that low concentrations of β-naphthol or pyrogallol inhibit the normal peroxidation of tetrahydrocarbazole, thus behaving as in other chain oxidations.

There is an interesting analogy between the effect of substituents on tetrahydrocarbazole peroxidations, and on the obviously similar autoxidations of phenylhydrazones (Pausacker, *J.*, 1950, 3478). Both types of oxidation probably depend on the initial homolysis of a nitrogen–hydrogen bond, with the formation of a nitrogen free radical, where the undissociated molecule, with an electron-donating group, is relatively less stable than when it has an electron-attracting substituent which can interact, through the ring, with the unshared pair of electrons on the nitrogen atom. Similar considerations apply to the dissociation of tetra-arylhydrazines into diarylamino-radicals studied by Wieland and his co-workers (see, *e.g.*, *Ber.*, 1915, **48**, 1078). Here, also, dissociation is favoured by substituents such as methoxyl and dimethylamino, but inhibited by electron-attracting substituents.

The failure of 1 : 2 : 3 : 4-tetrahydro-6-hydroxycarbazole to peroxidise in organic solvents has already been noted. A solution of this compound in dilute aqueous alkali, however, was rapidly attacked by air, becoming yellow and acquiring oxidising properties since it liberated iodine from acidified potassium iodide solution. When the oxidation was carried out quantitatively, it was found that two atoms of oxygen were taken up per molecule of the phenol and the oxidising agent formed was equivalent to 1·75 atoms of iodine, but despite the fairly precise stoicheiometry of the reaction, suggesting that a homogeneous product is formed in the first instance, we have been unable so far to isolate a pure oxidation product. The solution gave a negative test for hydrogen peroxide with titanic sulphate, and the oxidising agent formed was not volatile in steam.

Of the tetrahydrocarbazoles used in this study, only 1 : 2 : 3 : 4-tetrahydro-6-hydroxycarbazole and its benzyl ether were new. Several methods for the preparation of the phenol were investigated; demethylation of 1 : 2 : 3 : 4-tetrahydro-6-methoxycarbazole with aluminium bromide in boiling toluene gave only a small yield of the compound whilst attempts to convert 6-amino-1 : 2 : 3 : 4-tetrahydrocarbazole into the phenol by way of the diazonium salt were unsuccessful. The compound was ultimately obtained in good yield by the hydrogenolysis of 6-benzyloxy-1 : 2 : 3 : 4-tetrahydrocarbazole which was formed

by the interaction of *cyclo*hexanone with *p*-benzyloxyphenylhydrazine in boiling acetic acid.

Experimental

Autoxidation of 5 : 6 : 7 : 8-*Tetrahydrocarbazolecarboxylic Acids.*—A slow stream of air was aspirated through a solution of 5 : 6 : 7 : 8-tetrahydrocarbazole-4-carboxylic acid (Plant and Collar, *J.*, 1926, 808) (2·0 g.) in 5% aqueous sodium hydroxide (100 ml.) for 48 hours and the yellow mixture acidified with dilute sulphuric acid. The resulting yellow precipitate (1·8 g.) was separated into an alcohol-insoluble (A) (0·2 g.) and an alcohol-soluble fraction (B). From (A) 4-*hydroxy*-2 : 3-cyclo*pentenoquinoline*-5-*carboxylic acid* was isolated as a white infusible microcrystalline powder by dissolution in alkali and reprecipitation, followed by repeated washing with methanol (Found : C, 67·9; H, 5·0; N, 6·3. $C_{13}H_{11}O_3N$ requires C, 68·1; H, 4·8; N, 6·1%). This compound, which is very sparingly soluble in the usual organic solvents, could not be recrystallised : light absorption (in phosphate buffer, pH = 8), $\lambda_{max.}$ 240, 319, 333 mμ (log ε = 4·53, 4·07, 4·08); $\lambda_{min.}$ 267 mμ (log ε = 3·14). Crystallised from acetic acid fraction (B) gave cyclo*pentane*spiro-2-ψ-*indoxyl*-4-*carboxylic acid* in short golden rods (0·3 g.), m. p. 227° (decomp.) (Found : C, 67·9; H, 5·9; N, 6·3. $C_{13}H_{13}O_3N$ requires C, 67·5; H, 5·7; N, 6·1%). An alcoholic solution of this acid exhibited a strong green fluorescence; light absorption in ethanol, $\lambda_{max.}$ 258, 434 mμ (log ε 4·11, 3·63); $\lambda_{min.}$ 335 mμ (log ε 2·26).

Further concentration of the alcoholic liquor after the isolation of the *spiro*indoxyl gave an intractable gum from which only traces of unchanged tetrahydrocarbazole-4-carboxylic acid could be isolated.

By the same procedure aeration of 5 : 6 : 7 : 8-tetrahydrocarbazole-3-carboxylic acid (Plant and Collar, *loc. cit.*) (2 g.), in 5% aqueous sodium hydroxide (150 ml.), for 48 hours gave the sparingly soluble 4-*hydroxy*-2 : 3-cyclo*pentenoquinoline*-6-*carboxylic acid* which was purified by recrystallisation of its sodium salt from 10% aqueous sodium chloride. Regenerated therefrom, the acid was obtained as a white microcrystalline powder which did not melt below 360° and was almost insoluble in the usual solvents (Found : C, 68·2; H, 4·9; N, 6·2%). Light absorption (in phosphate buffer, pH = 8) : $\lambda_{max.}$ 255, 315, 332 mμ (log ε 4·37, 3·90, 3·83); $\lambda_{min.}$ 277 mμ (log ε 3·16). By crystallisation from acetic acid the alcohol-soluble fraction of the crude product gave unchanged 5 : 6 : 7 : 8-tetrahydrocarbazole-3-carboxylic acid (0·4 g.); the accompanying yellow fluorescent substance remaining in the acetic acid liquors could not be isolated.

Similarly, 5 : 6 : 7 : 8-tetrahydrocarbazole-2-carboxylic acid (2 g.) (Plant and Collar, *loc. cit.*) furnished 4-*hydroxy*-2 : 3-cyclo*pentenoquinoline*-7-*carboxylic acid* (0·4 g.) and unchanged starting material (1·2 g.), contaminated by a trace of a fluorescent substance. Purified by reprecipitation from its alkaline solution, the quinoline acid was a white microcrystalline powder, m. p. >360° (Found : C, 67·9; H, 4·9; N, 6·1%). Light absorption (in phosphate buffer, pH = 8) : $\lambda_{max.}$ 251, 326 mμ (log ε 4·36, 3·74); $\lambda_{min.}$ 280 mμ (log ε 3·20).

After having been aerated for 3 days a solution of 5 : 6 : 7 : 8-tetrahydrocarbazole-1-carboxylic acid (2 g.) (Plant and Collar, *loc. cit.*) did not yield a product insoluble in alcohol (yield of acid recovered after purification, 1·7 g.).

5-*Carbomethoxy*-1 : 2 : 3 : 4-*tetrahydrocarbazol*-11-*yl Hydroperoxide.*—On being kept in an open vessel for 2 days a solution of methyl 5 : 6 : 7 : 8-tetrahydrocarbazole-4-carboxylate (Plant and Collar, *loc. cit.*) (1·2 g.) in benzene (10 ml.) deposited pale yellow prisms (1·1 g.) of the *hydroperoxide* which was rapidly recrystallised from methanol, forming glistening colourless needles, m. p. 149—150° (decomp. with green flash) (Found : C, 64·3; H, 5·7; N, 5·4. $C_{14}H_{15}O_4N$ requires C, 64·4; H, 5·8; N, 5·4%). This compound, which is readily soluble in dilute mineral acids or aqueous alkalis, liberated the theoretical amount of iodine from acidified aqueous potassium iodide. A solution of the hydroperoxide (0·7 g.) in N-sodium hydroxide (30 ml.) which had been kept for 3 days and then acidified gave a precipitate which was extracted with boiling alcohol (15 ml.). Purification of the insoluble acidic residue (0·5 g.) with aqueous alkali, followed by washing with methanol, gave 4-hydroxy-2 : 3-*cyclo*pentenoquinoline-5-carboxylic acid, identified by comparison of its general properties and absorption with those of an authentic specimen (Found : N, 5·7%). Evaporation of the alcoholic extract of the crude product gave a little *cyclo*pentane*spiro*-2-ψ-indoxyl-4-carboxylic acid, m. p. and mixed m. p. 227° (decomp.) after purification from acetic acid.

A solution of the hydroperoxide (0·7 g.) in ether (100 ml.) was agitated with 20% aqueous sodium sulphite (20 ml.) for 8 hours, the ethereal layer was separated, the sulphite liquor was extracted several times with ether, and the combined ethereal solutions were evaporated,

leaving a pale yellow gum which was extracted with boiling light petroleum (b. p. 60—80°) (10 ml.). On cooling this extract deposited colourless plates (150 mg.), m. p. 92—95°, a portion (50 mg.) of which was heated under reflux with 5% methanolic potassium hydroxide (3 ml.) for 1 hour. On acidification the cooled hydrolysate gave *cyclo*pentane*spiro*-2-ψ-indoxyl-4-carboxylic acid, forming yellow rods (37 mg.), m. p. and mixed m. p. 227° (decomp.), from acetic acid.

6-*Carbomethoxy*-1 : 2 : 3 : 4-*tetrahydrocarbazol*-11-*yl Hydroperoxide*.—On being kept for 3 days a solution of methyl 5 : 6 : 7 : 8-tetrahydrocarbazole-3-carboxylate (0·2 g.) in a mixture of benzene (5 ml.) and light petroleum (b. p. 60—80°) (3 ml.) deposited the *hydroperoxide* as a sticky semi-crystalline solid. Crystallisation of the combined products from five experiments gave colourless needles (0·12 g.), m. p. 136° (decomp.) (Found : C, 64·4; H, 5·9; N, 5·1%).

1 : 2 : 3 : 4-*Tetrahydro*-6-*methoxycarbazol*-11-*yl Hydroperoxide*.—Prepared according to Borsche *et al.* (*Annalen*, 1908, **359**, 52), who give m. p. 94—95°, 1 : 2 : 3 : 4-tetrahydro-6-methoxycarbazole had m. p. 104—105° after purification from methanol (Found : C, 77·4; H, 7·3; N, 6·8. Calc. for $C_{13}H_{15}ON$: C, 77·6; H, 7·5; N, 7·0%).

On being kept in an open flask for 24 hours a solution of this carbazole (0·7 g.) in light petroleum (b. p. 60—80°) (100 ml.) deposited 1 : 2 : 3 : 4-*tetrahydro*-6-*methoxycarbazol*-11-*yl hydroperoxide* (0·5 g.) which separated from ethyl acetate–light petroleum (b. p. 60—80°) in clusters of shining pale green blades, m. p. 126° (vigorous decomp.), having the properties expected of a hydroperoxide (Found : C, 67·3; H, 6·6; N, 6·3. $C_{13}H_{15}O_3N$ requires C, 66·9; H, 6·5; N, 6·0%).

Rates of Peroxidation of Substituted Tetrahydrocarbazoles.—One m-mole of each tetrahydrocarbazole was dissolved by agitation with " AnalaR " benzene (100 ml.; freshly distilled over sodium) and the time noted. Aliquot portions (10 ml.) of solution were removed at intervals and added to 2N-sulphuric acid (100 ml.), followed by " AnalaR " potassium iodide (1 g.), the mixture was kept in the dark for 5 minutes, and the liberated iodine was estimated with 0·01M-sodium thiosulphate. Applied to tetrahydrocarbazolyl hydroperoxide, this method gave titres of 95—99%. Where benzoyl peroxide was employed as a catalyst (2 ml. of 0·05M were used) consistent peroxidation curves were obtained in duplicate runs with tetrahydrocarbazole, and preliminary experiments showed that benzoyl peroxide did not liberate iodine from potassium iodide under the conditions used in estimating peroxide values.

6-*Bromo*-1 : 2 : 3 : 4-*tetrahydrocarbazol*-11-*yl Hydroperoxide*.—This compound separated in rosettes of long colourless rods (0·5 g.), m. p. 136—137° (decomp.), from an exposed solution of 6-bromo-1 : 2 : 3 : 4-tetrahydrocarbazole (Borsche *et al.*, *loc. cit.*) (0·8 g.) in a mixture of benzene (20 ml.) and light petroleum (b. p. 60—80°) (100 ml.). Recrystallised from ethyl acetate–light petroleum the *hydroperoxide* formed short rods (0·3 g.), m. p. 148° (decomp.) (Found : C, 51·6; H, 4·3; N, 5·1; Br, 27·6. $C_{12}H_{12}O_2NBr$ requires C, 51·0; H, 4·3; N, 5·0; Br, 28·4%).

6-*Acetamido*-1 : 2 : 3 : 4-*tetrahydrocarbazol*-11-*yl hydroperoxide* separated in minute grey prisms (0·46 g.), m. p. 154° (decomp.), from an exposed solution of 6-acetamido-1 : 2 : 3 : 4-tetrahydrocarbazole (Perkin and Plant, *J.*, 1921, **119**, 1825) (0·5 g.) in benzene, and on recrystallisation from dioxan– or benzene–light petroleum had m. p. 165° (decomp.) (Found : C, 65·0; H, 6·1; N, 10·7. $C_{14}H_{16}O_3N_2$ requires C, 64·6; H, 6·2; N, 10·8%).

6-*Benzyloxy*-1 : 2 : 3 : 4-*tetrahydrocarbazole*.—4-Benzyloxyaniline hydrochloride (Blanksma, *Rec. Trav. chim.*, 1909, **28**, 105) (13 g.), suspended in water (100 ml.) and hydrochloric acid (150 ml.) at below 0°, was diazotised with sodium nitrite (3·8 g.) in water (20 ml.) (agitate). 70 Minutes later stannous chloride (32 g. of dihydrate), in concentrated hydrochloric acid (50 ml.), was added to the diazonium solution kept at $< -8°$ and the resulting 4-*benzyloxyhydrazine hydrochloride* collected and recrystallised from alcohol, forming shining colourless plates (9·5 g.), m. p. 194—196° (decomp.) (Found : C, 62·6; H, 6·0; N, 10·8. $C_{13}H_{14}ON_2,HCl$ requires C, 62·3; H, 6·0; N, 11·2%). Agitated with 2N-sodium hydroxide (200 ml.) for 2 hours, the hydrochloride gave the free base, which was collected, washed with water, and dried. When a solution of this product in acetic acid (30 ml.) containing *cyclo*hexanone (4 g.) was heated under reflux for 15 minutes and cooled, the resulting 6-*benzyloxy*-1 : 2 : 3 : 4-*tetrahydrocarbazole* separated in light tan needles (2·5 g.), m. p. 135—136°. It formed colourless needles, m. p. 136—137°, from benzene–light petroleum (Found : C, 82·0; H, 6·9; N, 4·8. $C_{19}H_{19}ON$ requires C, 82·3; H, 6·9; N, 5·1%).

1 : 2 : 3 : 4-*Tetrahydro*-6-*hydroxycarbazole*.—Demethylation of 1 : 2 : 3 : 4-tetrahydro-6-methoxycarbazole (1 g.) with aluminium bromide (2·7 g.) in boiling toluene (30 ml.) for ½ hour, followed by the addition of ice and concentrated hydrochloric acid to the cooled reaction

mixture, gave 1 : 2 : 3 : 4-*tetrahydro*-6-*hydroxycarbazole* which was isolated with ether and purified by crystallisation from benzene–light petroleum, forming colourless blades (0·25 g.), m. p. 172—173° (since recorded by Milne and Tomlinson, *J.*, 1952, 2789). Sublimed in a high vacuum, the compound had m. p. 179° (Found : C, 76·7; H, 6·9; N, 7·5. $C_{12}H_{13}ON$ requires C, 77·0; H, 7·0; N, 7·5%). The same phenol, m. p. and mixed m. p. 179°, was obtained in almost quantitative yield by hydrogenolysis of the 6-benzyloxy-1 : 2 : 3 : 4-tetrahydrocarbazole in methanol with hydrogen and palladium–charcoal in the usual manner. It was sparingly soluble in water and easily soluble in aqueous sodium hydroxide, giving a colourless solution which rapidly became yellow.

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[*Received, July 29th*, 1952.]