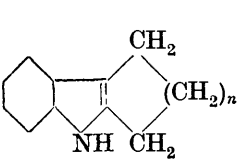
XV.—*The Action of Nitric Acid on Polycyclic Indole Derivatives. Part IX.**

By Stephen Arnold Bryant and Sydney Glenn Preston Plant.

In view of the widely different nature of the products obtained when nitric acid acts on the acyl derivatives of tetrahydrocarbazole (I; $n = 2$), dihydropentindole (I; $n = 1$), 7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole (II), and 8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole (III; R = H), and of the deep-seated variations observed in the reactions of substances formed in such cases by the addition of OH and NO_2 or OH and OH to the double linkage (see the previous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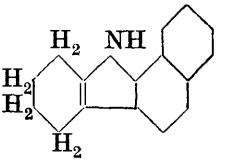
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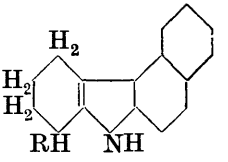
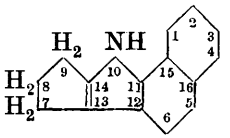

(III.)

papers in this series), it became of interest to extend these investigations to certain closely related types. For this purpose 7 : 8-*dihydro-αβ-naphthapentindole* (IV) has now been prepared by an application of Fischer's indole synthesis to cyclo*pentanone-α-naphthylhydrazone*. When a solution of (IV) in acetic anhydride containing a few drops of concentrated sulphuric acid was boiled for several hours, two isomeric acetyl derivatives were formed. One of these (m. p. 157°) was evidently the expected 10-*acetyl* compound, since it was readily hydrolysed by aqueous-alcoholic potassium hydroxide with the regeneration of the indole (IV). The other (m. p. 215°) contained the acetyl group attached to a benzene nucleus, a fact which was confirmed by its stability towards aqueous-alcoholic potassium hydroxide and by conversion into an *oxime*, and, of the various possibilities for the location of this group, the 1-position seems the most probable for reasons which are discussed below.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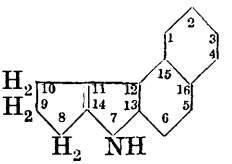
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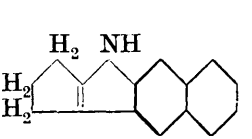
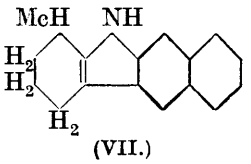

(VI.)

* The following communications are regarded as constituting the preceding parts of this series :—J., 1921, **119**, 1825; 1923, **123**, 676, 3242; 1926, 2260; 1928, 1840, 2454; 1929, 1970, 2493.

The formation of this 1(?)-*acetyl* compound was not due to an isomeric change involving the 10-acetyl derivative, since the latter was found to be completely unchanged after boiling with acetic anhydride and a little sulphuric acid. Efforts to obtain crystalline products by the action of nitric acid on the 10-acetyl compound in glacial acetic acid have been unsuccessful, and it has also not been found possible to benzoylate (IV) under the many conditions investigated.

9 : 10-*Dihydro-α′β′-naphthapentindole* (V), isomeric with (IV), was accordingly prepared by the Fischer method from cyclo*pentanone*-β-*naphthylhydrazone*. The alternative course for this reaction, which would give the substance (VI), cannot be considered with any justification as a possibility, since ring closure would involve the β-position in the naphthalene molecule. Moreover, the analogous reaction with *cyclo*hexanone-β-naphthylhydrazone has been proved conclusively by Oakeshott and Plant (J., 1928, 1840) to lead to the compound (III; R = H). It has, however, been stated recently by Cecchetti and Ghigi (*Gazzetta*, 1930, **60**, 185) that the Fischer reaction with 2-methyl*cyclo*hexanone-β-naphthylhydrazone yields two products, isolated as oils and analysed in the form of their picrates (m. p.'s 190° and 162—163°), which are regarded without any proof as the indole (VII) and the indolenine (VIII) respectively. Although it is extremely unlikely that these formulæ correctly represent the products of Cecchetti and Ghigi, nevertheless, in view of the desirability of removing any possible doubt concerning the nature of the compound (V), it was decided to examine their validity. It was found that the action of dilute sulphuric acid on 2-methyl*cyclo*hexanone-β-naphthylhydrazone yielded two solid pro-



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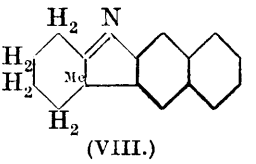

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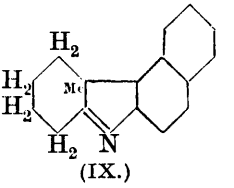


(IX.)

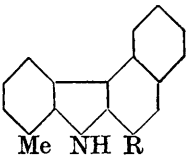
ducts, m. p.'s 115° and 92°, which are undoubtedly 8-methyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole (III; R = Me) (picrate, m. p. 201°, decomp.) and 12-methyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazolenine (IX) (picrate, m. p. 166°) respectively. The constitution assigned to the former was established by dehydrogenation, which led to 8-*methyl-α′β′-naphthacarbazole* (X; R = H), the identity of which was confirmed by an unambiguous synthesis. For this purpose a method analogous to that used by Schöpff (*Ber.*, 1896, **29**, 265) for the preparation of **α′β′-naphtha-**

carbazole was employed. 2-Hydroxy-3-naphthoic acid and *o*-tolylhydrazine were mixed in ethereal solution, and the resulting solid was heated until a reaction set in; ammonia was then evolved and 8-methyl-α′β′-naphthacarbazole-6-carboxylic acid (X; R = CO_2H) was formed. The latter, on decarboxylation, yielded 8-methyl-α′β′-naphthacarbazole, identical with the product just described. It is, therefore, obviously not justifiable to assume ring closure in the β-position in such reactions, and there can now be no reasonable doubt concerning the nature of (IX) and of (V).

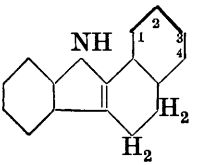
When the indole (V) was treated in acetone solution with acetyl chloride and aqueous sodium hydroxide (compare Stevens and Tucker, J., 1923, **123**, 2140), 7-*acetyl*-9 : 10-*dihydro*-α′β′-*naphthapentindole* was obtained, and the position of the acetyl group was confirmed by the readiness with which (V) was regenerated with alcoholic potassium hydroxide. On boiling a solution of this product in acetic anhydride containing a little sulphuric acid, further acetylation took place to give 5(?) : 7-*diacetyl*-9 : 10-*dihydro*-α′β′-*naphthapentindole*. The same diacetyl compound was obtained directly from (V) by boiling its solution in acetic anhydride and a trace of sulphuric acid. The reactions of this latter product indicate quite definitely that the second acetyl group is attached to a carbon atom, but its exact location is not certain, the 5-position being regarded as the most probable, since it represents an α-position in the naphthalene system and direct substitution into acylated dihydropentindoles has been shown to result in the introduction of the group into a meta-position with respect to the nitrogen atom (see Part VIII). Hydrolysis of the diacetyl compound with aqueous-alcoholic potassium hydroxide gave 5(?)-*acetyl*-9 : 10-*dihydro*-α′β′-*naphthapentindole*, which could be re-acetylated in acetone solution with acetyl chloride and aqueous sodium hydroxide or converted into 5(?)-*acetyl*-7-*benzoyl*-9 : 10-*dihydro*-α′β′-*naphthapentindole* by a similar process using benzoyl chloride. Treatment of (V) itself in acetone solution with benzoyl chloride and aqueous alkali gave the 7-*benzoyl* compound, and, by using ethyl chloroformate instead of benzoyl chloride, the 7-*carbethoxy*-compound was obtained. These two acyl derivatives could readily be hydrolysed to the original indole (V).

The 7-acetyl, 7-benzoyl, and 7-carbethoxy-derivatives of (V), when nitrated in glacial acetic acid solution under experimental conditions which in every case must be carefully followed, yielded each a *mononitro*-compound, and these, on hydrolysis, all gave the same *nitro*-9 : 10-*dihydro*-α′β′-*naphthapentindole*. It is established, therefore, that in all these compounds the nitro-group occupies the same position, which, for the reasons cited above in the case of the

5(?) : 7-diacetyl derivative, is believed to be on the 5-carbon atom. From the 7-carbethoxy-derivative of (V) it was possible also to obtain a *dinitro*-compound under the conditions described in the experimental section, but in all these processes of nitration it was not possible to isolate any crystalline products if the conditions employed differed seriously from those given. Furthermore, in no case was any indication found of the formation of a product through the addition of OH and NO_2 or OH and OH at the double linkage. A similar failure to isolate such addition products has been recorded in Part V (J., 1928, 1840), which deals with the derivatives of the naphthacarbazoles (II) and (III; R = H). In view of the fact that these addition products are very readily formed and easily isolated from the acyl derivatives of tetrahydrocarbazole (I; $n = 2$) and dihydropentindole (I; $n = 1$), it is remarkable that no single example of such a product has been found among the compounds derived from any of these four more complex types, which differ from the two simpler ones (I) only in having a second benzene nucleus attached to the one already present. These results indicated that it would be of interest to extend the investigations to substances which are derived from tetrahydrocarbazole or dihydropentindole by inserting a benzene nucleus in the reduced portion of the molecule.



(X.)



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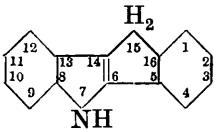
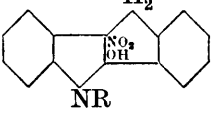


(XII.)

For this purpose 5 : 6-dihydro-αβ-naphthacarbazole (XI) and benzopentindole (XII) have been prepared by applying Fischer's indole synthesis to the phenylhydrazones of 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene and α-hydrindone respectively. The former reaction has recently been described by Ghigi (*Gazzetta*, 1930, **60**, 194), and the product (XI) has been previously obtained by Titley (J., 1928, 2571) from ethyl 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate by heating with phenylhydrazine hydrochloride and concentrated hydrochloric acid, and called "1 : 2-indolo(2 : 3)-3 : 4-dihydronaphthalene." It has now been found that the preparation of *N*-acyl derivatives from (XI) is surprisingly difficult and so far these have not been characterised. When, however, a solution of the substance in acetic anhydride containing a few drops of sulphuric acid was boiled for several hours, a monoacetyl derivative was formed, but the reactions of this product indicated that it is a *C*-acetyl compound. Thus it was quite unchanged when its solution

in alcoholic potassium hydroxide was boiled for 1½ hours, and, furthermore, it was found possible to prepare an *oxime* from it. This ketone closely resembles 1(?)-acetyl-7 : 8-dihydro-αβ-naphthapentindole, described above, and it seems probable that the acetyl groups occupy analogous positions in the two structures. If this is so, only the 1- and 4-positions are reasonable possibilities, and 1- is preferred, since the steric effects of the 1-acetyl group in the dihydro-αβ-naphthapentindole derivative could explain the inability to acetylate it further. The product derived from (XI) is called, therefore, 1(?)-*acetyl*-5 : 6-*dihydro*-αβ-*naphthacarbazole*. The inability to effect *N*-acylation of (XI) has prevented the further investigation of this substance along the desired lines.

The preparation of benzopentindole (XII) by the Fischer reaction has already been described by Hausmann (*Ber.*, 1889, **22**, 2022), Kipping (J., 1894, **65**, 494), and Leuchs and Kowalski (*Ber.*, 1925, **58**, 2825), and called "*o*-benzyleneindole," while Titley (*loc. cit.*), who prepared it from ethyl 1-hydrindone-2-carboxylate, has assigned to it the name "2 : 3-indeno(1 : 2)-indole." Leuchs and Kowalski have also prepared the 7-acetyl derivative, but it has not been found possible in the present work to prepare any crystalline substance from this by the action of nitric acid under various conditions. When benzopentindole was treated in acetone with benzoyl chloride and aqueous potassium hydroxide, it was converted into 7-*benzoyl-benzopentindole*, which could readily be hydrolysed with the regeneration of (XII). From the product of the action of nitric acid on this benzoyl compound in acetic acid it was possible to isolate a substance which had been formed by the addition of nitric acid, and closely resembled the analogous products isolated in the tetrahydrocarbazole and dihydropentindole series. This derivative must therefore be regarded as 14-*nitro*-6-*hydroxy*-7-*benzoyl*-6 : 14-*dihydrobenzopentindole* (XIII; R = Bz). The addition products of



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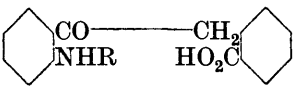

(XIV.)

this type previously obtained differ considerably in their behaviour towards alkalis. The present example readily dissolved in warm aqueous potassium hydroxide, and, after acidification with acetic acid, the main product of the reaction proved to be 14-*nitro*-6-*hydroxy*-6 : 14-*dihydrobenzopentindole* (XIII; R = H). In this respect the compound (XIII; R = Bz) behaves like the analogous derivative from 8-acetyldihydropentindole (Part VIII; J., 1929, 2493),

although an examination of the product indicated the probable presence of small quantities, insufficient for characterisation, of the acids (XIV; R = Bz) and (XIV; R = H) formed by the alternative reactions already observed in the earlier work.

In view of the remarkable differences in the reactions of derivatives of tetrahydrocarbazole on the one hand and dihydropentindole on the other (described in the earlier Parts) it became of interest to extend these investigations to 2 : 3 : 4 : 5-tetrahydroheptindole (I; $n = 3$), but so far attempts to acylate this substance have been unsuccessful, although similar conditions in the two former cases readily accomplished the desired process.

EXPERIMENTAL.

7 : 8-*Dihydro-αβ-naphthapentindole and its Acetylation Products.*—cyclo*Pentanone-α-naphthylhydrazone*, formed when α-naphthylhydrazine (50 g.) and *cyclo*pentanone (50 c.c.) were heated together on the steam-bath for 5 minutes, crystallised from alcohol in colourless prisms, m. p. 95° (Found : N, 12·3. $C_{15}H_{16}N_2$ requires N, 12·5%).

The crude hydrazone was heated together with water (1075 c.c.) and concentrated sulphuric acid (65 c.c.) on the steam-bath for 15 minutes with frequent shaking. The solid product was then crystallised from alcohol, 7 : 8-*dihydro-αβ-naphthapentindole* being obtained in long colourless prisms, m. p. 167° (Found: N, 6·5. $C_{15}H_{13}N$ requires N, 6·8%). Alternatively, a solution of the crude hydrazone in glacial acetic acid (200 c.c.) was boiled for a few minutes; the indole separated, on cooling, in colourless plates, m. p. 167°. When equal weights of the indole and picric acid were mixed in hot benzene, the picrate separated in reddish-brown needles, m. p. 167° (decomp.).

A solution of the indole (50 g.) in acetic anhydride (200 c.c.) and a few drops of concentrated sulphuric acid was boiled under reflux for 10 hours; most of the acetic anhydride was then distilled off at the ordinary pressure and the residue was distilled at a pressure of 40 mm. Four fractions with the following b. p.'s were collected, (i) 288—291°, (ii) 291—296°, (iii) 296—300°, and (iv) 300—320°. When the first fraction was crystallised successively from glacial acetic acid and alcohol, 10-*acetyl*-7 : 8-*dihydro-αβ-naphthapentindole* was obtained in colourless plates, m. p. 157° (Found: N, 5·7. $C_{17}H_{15}ON$ requires N, 5·6%). The second fraction consisted mainly of the unchanged indole, and the third and fourth fractions were crystallised from alcohol and ethyl acetate respectively. After the latter two products had been united and recrystallised from chloroform, 1(?)-*acetyl*-7 : 8-*dihydro-αβ-naphthapentindole* was isolated in

yellow prisms, m. p. 215° (Found: C, 81·7; H, 6·1; N, 5·7. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·0; N, 5·6%).

When a mixture of the 10-acetyl derivative (1 g.), potassium hydroxide (3 g.), water (5 c.c.), and alcohol (20 c.c.) was boiled for ½ hour, then diluted with a little water and allowed to cool, 7 : 8-dihydro-αβ-naphthapentindole separated in good yield. After a similar solution of the 1(?)-acetyl derivative in aqueous-alcoholic potassium hydroxide had been boiled for 4 hours, the unchanged substance separated quantitatively on cooling. When a mixture of the 1(?)-acetyl compound (1 g.), hydroxylamine hydrochloride (2·5 g.), crystallised sodium acetate (3·5 g.), and alcohol (25 c.c.) was boiled for an hour and then diluted with water, the *oxime* was precipitated; it crystallised from ethyl acetate in colourless plates, m. p. 236° (decomp.) (Found: N, 10·5. $C_{17}H_{16}ON_2$ requires N, 10·6%).

9 : 10-*Dihydro-α'β'-naphthapentindole and its Acyl Derivatives.*—When a mixture of β-naphthylhydrazine (20 g.) and *cyclo*pentanone (20 c.c.) was heated on the steam-bath for 5 minutes, the *hydrazone* was formed as an oil; this solidified in contact with petroleum and then crystallised from methyl alcohol in colourless prisms (slowly decomposing on exposure to light), m. p. 77° (Found: N, 12·9. $C_{15}H_{16}N_2$ requires N, 12·5%). The crude hydrazone was treated with water (430 c.c.) and concentrated sulphuric acid (25 c.c.), and the mixture heated on the steam-bath for ½ hour with frequent shaking. The aqueous liquid was then removed by decantation from the sticky brown product, which was washed with water and subsequently obtained as a solid (22 g., m. p. 100°) by crystallisation from petroleum (800 c.c., b. p. 80—100°). After recrystallisation from alcohol, 9 : 10-*dihydro-α'β'-naphthapentindole* was isolated in colourless plates, m. p. 103° (Found: N, 6·7. $C_{15}H_{13}N$ requires N, 6·8%). The corresponding picrate separated from a relatively large amount of alcohol in brown needles, m. p. 189° (decomp.).

(a) *Acetyl derivatives.* A mixture of the indole (6 g.), acetone (80 c.c.), and aqueous sodium hydroxide (30 g. of 50%) was treated gradually with acetyl chloride (20 c.c.) with vigorous shaking and occasional cooling. After dilution with water, the solid product was collected and washed first with water and then with acetone. The 7-*acetyl*-9 : 10-*dihydro-α'β'-naphthapentindole* obtained was practically pure, but it could be recrystallised from xylene, from which it separated in colourless prisms, m. p. 170° (Found: N, 5·7. $C_{17}H_{15}ON$ requires N, 5·6%). When a solution of the 7-acetyl derivative in alcoholic potassium hydroxide was boiled for ½ hour and then diluted with water, 9 : 10-dihydro-α'β'-naphthapentindole was precipitated.

A solution of the 7-acetyl derivative (2 g.) in acetic anhydride (20 c.c.) containing two drops of concentrated sulphuric acid was boiled for ½ hour; on cooling, a dark green solid separated. This product was washed with acetic acid and crystallised successively from *cyclo*hexanone and *cyclo*pentanone, 5(?) : 7-*diacetyl*-9 : 10-*dihydro*-α′β′-*naphthapentindole* being obtained in pale green plates, m. p. 234° (Found: N, 4·9. $C_{19}H_{17}O_2N$ requires N, 4·8%). The same diacetyl derivative was isolated from a similar process after a solution of 9 : 10-dihydro-α′β′-naphthapentindole (10 g.) in acetic anhydride (100 c.c.) containing concentrated sulphuric acid (0·3 c.c.) had been boiled for 2 hours under reflux.

When a mixture of the 5(?) : 7-diacetyl derivative (5 g.), potassium hydroxide (7 g.), water (10 c.c.), and alcohol (130 c.c.) was boiled for ½ hour and then allowed to cool, 5(?)-*acetyl*-9 : 10-*dihydro*-α′β′-*naphthapentindole* separated, a further quantity being obtained by concentrating the mother-liquor. After recrystallisation from amyl alcohol it was isolated in greenish-yellow plates, m. p. 239° (Found: N, 5·7. $C_{17}H_{15}ON$ requires N, 5·6%). On the gradual addition of acetyl chloride (5 c.c.) to a mixture of the 5(?)-acetyl compound (1·5 g.), acetone (60 c.c.), and aqueous sodium hydroxide (8 g. of 50%), followed by dilution with water, the 5(?) : 7-diacetyl derivative (purified by crystallisation from *cyclo*hexanone) was regenerated. By an analogous process with the aid of benzoyl chloride and potassium hydroxide, the 5(?)-acetyl compound was converted into 5(?)-*acetyl*-7-*benzoyl*-9 : 10-*dihydro*-α′β′-*naphthapentindole*, which, after successive crystallisation from *cyclo*hexanone and xylene, was obtained in pale greenish-yellow plates, m. p. 163° (Found: N, 3·9. $C_{24}H_{19}O_2N$ requires N, 4·0%). After a mixture of this product (1 g.), potassium carbonate (3 g.), water (75 c.c.), and alcohol (150 c.c.) had been boiled for 1½ hours, and the solution filtered and cooled, 5(?)-acetyl-9 : 10-dihydro-α′β′-naphthapentindole separated.

(b) *Benzoyl derivative.* Benzoyl chloride (15 c.c.) was added with shaking to a mixture of 9 : 10-dihydro-α′β′-naphthapentindole (9 g.), acetone (80 c.c.), and aqueous potassium hydroxide (22 g. of 66%), and, after the addition of water, the product was washed with acetone and crystallised from acetic anhydride, 7-*benzoyl*-9 : 10-*dihydro*-α′β′-*naphthapentindole* being obtained in pale yellow prisms, m. p. 196° (Found: N, 4·8. $C_{22}H_{17}ON$ requires N, 4·5%). Hydrolysis of this product to the original indole was best effected by boiling it (1 g.) with potassium carbonate (3 g.), water (50 c.c.), and alcohol (65 c.c.) for an hour. After the solution had been filtered hot and diluted with water, the indole was precipitated in a practically pure condition.

(c) *Carbethoxy-derivative.* Prepared by a process analogous to that described for the benzoyl derivative, ethyl chloroformate being used instead of benzoyl chloride, *ethyl* 9 : 10-*dihydro*-α′β′-*naphthapentindole*-7-*carboxylate* crystallised from benzene in colourless prisms, m. p. 160° (Found : N, 4·9. $C_{18}H_{17}O_2N$ requires N, 5·0%). Hydrolysis to the original indole was effected by the action of boiling alcoholic potassium hydroxide for an hour, the product being isolated by the subsequent addition of water and crystallised from petroleum.

Nitration of the 7-*Acyl*-9 : 10-*dihydro*-α′β′-*naphthapentindoles.*— When a solution of 7-acetyl-9 : 10-dihydro-α′β′-naphthapentindole (2 g.) in glacial acetic acid (100 c.c.) at 70° was treated with nitric acid (1 c.c. of *d* 1·42), a bright yellow precipitate (1·1 g.) appeared; this was separated from the cooled mixture, washed with acetic acid, and crystallised from xylene, 5(?)-*nitro*-7-*acetyl*-9 : 10-*dihydro*-α′β′-*naphthapentindole* being obtained in lemon-yellow plates, m. p. 247° (Found : N, 9·5. $C_{17}H_{14}O_3N_2$ requires N, 9·5%). When a mixture of this substance (3 g.), potassium carbonate (12 g.), water (150 c.c.), and alcohol (195 c.c.) was boiled for an hour and allowed to cool, 5(?)-*nitro*-9 : 10-*dihydro*-α′β′-*naphthapentindole* separated; on recrystallisation from benzene, it was isolated in brick-red plates, m. p. 228° (Found : N, 11·0. $C_{15}H_{12}O_2N_2$ requires N, 11·1%). This product was re-acetylated when treated in acetone solution with aqueous sodium hydroxide and acetyl chloride.

7-Benzoyl-9 : 10-dihydro-α′β′-naphthapentindole (6 g.) was ground with a solution of nitric acid (3 c.c. of *d* 1·5) in glacial acetic acid (30 c.c.) and left for 6 hours with occasional stirring. The solid product was then collected, washed with acetic acid, and crystallised from chloroform, 5(?)-*nitro*-7-*benzoyl*-9 : 10-*dihydro*-α′β′-*naphthapentindole* (1·6 g.) being obtained in yellow plates, m. p. 259° (Found : C, 74·3; H, 4·6. $C_{22}H_{16}O_3N_2$ requires C, 74·2; H, 4·5%). When hydrolysed by the process already described for the corresponding acetyl derivative, it yielded 5(?)-nitro-9 : 10-dihydro-α′β′-naphthapentindole identical with the product mentioned above.

When a solution of ethyl 9 : 10-dihydro-α′β′-naphthapentindole-7-carboxylate (2 g.) in glacial acetic acid (100 c.c.) at 70° was treated with nitric acid (1 c.c. of *d* 1·42), a solid product separated almost immediately, but rapidly redissolved. The extent to which this phenomenon was observed varied considerably in several similar experiments. After the solution had become cold, the final product of the reaction began to separate. This was collected after a day and recrystallised from chloroform, *ethyl dinitro*-9 : 10-*dihydro*-α′β′-*naphthapentindole*-7-*carboxylate* being obtained in yellow plates, m. p. 220° (decomp.) (Found : C, 59·4; H, 4·2; N, 11·1. $C_{18}H_{15}O_6N_3$

requires C, 58·5; H, 4·1; N, 11·4%). In order to isolate a mononitro-compound from the above reaction a smaller quantity of nitric acid (0·75 c.c.) was used and the whole was rapidly cooled immediately after admixture. The solid was then collected, washed with acetic acid, and recrystallised from benzene, *ethyl* 5(?)-*nitro*-9 : 10-*dihydro*-α′β′-*naphthapentindole*-7-*carboxylate* being obtained in lemon-yellow plates, m. p. 202° (Found: N, 8·7. $C_{18}H_{16}O_4N_2$ requires N, 8·6%). This substance remained unchanged when treated with nitric acid in glacial acetic acid at 70°. When hydrolysed under conditions similar to those used for the corresponding acetyl derivative described above, it yielded 5(?)-nitro-9 : 10-dihydro-α′β′-naphthapentindole.

8-*Methyl*-8 : 9 : 10 : 11-*tetrahydro*-α′β′-*naphthacarbazole and* 12-*Methyl*-8 : 9 : 10 : 11-*tetrahydro*-α′β′-*naphthacarbazolenine*.—β-Naphthylhydrazine (20 g.) and 2-methyl*cyclo*hexanone (14 g.) were heated together on the steam-bath for ½ hour, and the oily hydrazone was then treated with water (300 c.c.) and concentrated sulphuric acid (50 c.c.). After being boiled for 10 minutes with frequent shaking, the mixture was diluted with water and extracted with ether. The ethereal solution was dried over calcium chloride, the solvent removed, and the residual dark red oil (15 g.) boiled in glacial acetic acid (100 c.c.) with charcoal for 5 minutes. After being filtered, the solution was concentrated under reduced pressure; on cooling and standing, 8-methyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole separated in practically colourless prisms, m. p. 113°. When recrystallised from petroleum (b. p. 60—80°), it was isolated in colourless prisms, m. p. 115° (Found: C, 86·7; H, 7·3. Calc.: C, 86·8; H, 7·2%). Its picrate separated from much alcohol in dark crimson needles, m. p. 201° (decomp.).

The dilute sulphuric acid solution from the indole synthesis was made alkaline by the addition of aqueous sodium hydroxide and extracted with ether. After the ethereal solution had been dried over potassium carbonate, and the solvent removed, a dark brown syrup (12·5 g.) remained. When this was distilled, a yellowish-brown oil (b. p. 228—232°/16 mm.) was collected, and, on treatment with petroleum (b. p. 60—80°), the product solidified. After being crystallised from this solvent, 12-methyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazolenine was obtained in colourless plates, m. p. 92° (Found: C, 87·1; H, 7·4. Calc.: C, 86·8; H, 7·2%). In admixture with the isomeric indole its m. p. was much depressed. This indolenine was readily soluble in dilute hydrochloric acid, from which it was reprecipitated by ammonia. Its picrate separated from alcohol in bright yellow prisms, m. p. 166°.

A mixture of the indole (III; R = Me) (4·7 g.), sulphur (1·3 g.),

and quinoline (30 c.c.) was boiled for 45 minutes, hydrogen sulphide being freely evolved during the early stages. After being cooled, the solution was poured into dilute hydrochloric acid; the yellow solid so obtained was dried in a desiccator and then distilled under reduced pressure with the addition of a small quantity of iron filings. The distillate was again distilled under similar conditions with iron filings, and the product then readily solidified. After crystallisation from glacial acetic acid, 8-*methyl-α′β′-naphthacarbazole* was obtained in colourless prisms, m. p. 144° (Found: C, 88·5; H, 5·7. $C_{17}H_{13}N$ requires C, 88·3; H, 5·6%).

Synthesis of 8-*Methyl-α′β′-naphthacarbazole.*—When ethereal solutions of 2-hydroxy-3-naphthoic acid (19 g.) and *o*-tolylhydrazine (12·5 g.) were mixed, a precipitate (22 g.), which presumably consisted of the hydrazine salt, separated almost immediately. This product was heated in a flask immersed in an oil-bath, and, when its temperature reached 130°, a reaction started. The temperature rose steadily to 165° and then very rapidly to 210°, a considerable amount of ammonia being evolved. On being cooled, the oily product solidified, and, after warming and stirring with alcohol, 8-methyl-α′β′-naphthacarbazole-6-carboxylic acid was obtained as an insoluble residue. It crystallised from glacial acetic acid in small yellow plates, m. p. 320°. The acid was readily soluble in aqueous sodium carbonate and was reprecipitated by the addition of dilute hydrochloric acid. When it was intimately mixed with an excess of pulverised soda-lime and strongly heated in a hard-glass test-tube, an oil collected and solidified, on cooling. This product was crystallised from acetic acid, 8-methyl-α′β′-naphthacarbazole being obtained in small colourless prisms, m. p. 142°. In admixture with a specimen of the product (m. p. 144°) obtained by the dehydrogenation of the indole (III; R = Me), its m. p. was 143°.

1(?)-*Acetyl*-5 : 6-*dihydro*-αβ-*naphthacarbazole.*—5 : 6-Dihydro-αβ-naphthacarbazole was prepared by heating 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (15 g.) and phenylhydrazine (11 g.) on a steam-bath for a few minutes and treating the resulting hydrazone with water (200 c.c.) and concentrated sulphuric acid (40 c.c.). After the mixture had been vigorously boiled for an hour, the product was crystallised from alcohol and obtained in colourless plates, m. p. 161° (compare Ghigi, *loc. cit.*). A solution of this indole (10 g.) in acetic anhydride (100 c.c.) containing a few drops of concentrated sulphuric acid was boiled under reflux for 6 hours. After the solution had been concentrated, the residual liquid was distilled under reduced pressure, and a product (b. p. about 370°/40 mm.) was collected; this was crystallised successively from alcohol and amyl acetate, 1(?)-*acetyl*-5 : 6-*dihydro*-αβ-*naphtha*-

carbazole being obtained in yellow plates, m. p. 253° (Found: C, 82·3; H, 5·5. $C_{18}H_{15}ON$ requires C, 82·8; H, 5·7%). This ketone was recovered quantitatively and unchanged after its solution in alcoholic potassium hydroxide had been boiled for 1½ hours. A small quantity (0·2 g.) was mixed with hydroxylamine hydrochloride (0·6 g.), crystallised sodium acetate (0·9 g.), and alcohol (10 c.c.), and the whole boiled for an hour; the *oxime*, obtained by dilution with water, crystallised from amyl acetate in colourless needles, m. p. 292° (decomp.) (Found: N, 9·8. $C_{18}H_{16}ON_2$ requires N, 10·1%).

Derivatives of Benzopentindole.—The benzopentindole was prepared by boiling a solution of α-hydrindonephenylhydrazone in alcoholic hydrogen chloride for 20 minutes, and separated in colourless plates, m. p. 258° (after recrystallisation from alcohol). Benzoyl chloride (6 c.c.) was added to a mixture of benzopentindole (3 g.), warm acetone (60 c.c.), and aqueous potassium hydroxide (7 g. of 60%), and, after being vigorously shaken, the whole was diluted with water; *7-benzoylbenzopentindole* then separated. It crystallised from benzene in pale yellow plates, m. p. 187° (Found: N, 4·4. $C_{22}H_{15}ON$ requires N, 4·5%). A solution of this benzoyl compound in alcoholic potassium hydroxide was boiled for ½ hour; benzopentindole separated on cooling. A solution of the benzoyl compound (3 g.) in glacial acetic acid (150 c.c.) at 70° was treated with nitric acid (3 c.c. of *d* 1·5) dissolved in a little acetic acid. After being cooled, the solution was concentrated to 10 c.c. under reduced pressure, and, on standing, a solid separated. This was washed with glacial acetic acid until colourless, dried over sodium hydroxide in a desiccator, and then extracted with boiling ether. The residue (1·4 g.), which consisted of *14-nitro-6-hydroxy-7-benzoyl-6 : 14-dihydrobenzopentindole*, melted at 169° (decomp.) and was unchanged by crystallisation from alcohol or benzene; it separated from the latter solvent in colourless needles (Found: C, 71·5; H, 4·5; N, 7·7. $C_{22}H_{16}O_4N_2$ requires C, 71·0; H, 4·3; N, 7·5%). When cautiously heated, this product decomposed with evolution of oxides of nitrogen, but after its solution in alcohol had been boiled for 1½ hours it crystallised unchanged on cooling. It dissolved completely when shaken for a few minutes with warm aqueous potassium hydroxide (20%), and the product, obtained on acidification with acetic acid, was purified first by crystallisation from alcohol, then by grinding with dilute hydrochloric acid to remove any traces of *o*-(*o*-aminobenzoylmethyl)benzoic acid (XIV; R = H), and finally by recrystallisation from alcohol, from which it separated in colourless prisms, m. p. 200° (decomp.) (Found: C, 67·7; H, 5·1; N, 8·7. $C_{15}H_{12}O_3N_2$ requires C, 67·2; H, 4·5;

N, 10·4%). There is little doubt that this product is essentially 14-*nitro*-6-*hydroxy*-6 : 14-*dihydrobenzopentindole*, but the analysis indicates the probable presence of a small amount of *o*-(*o*-benzamidobenzoylmethyl)benzoic acid (XIV; R = Bz) ($C_{22}H_{17}O_4N$ requires C, 73·5; H, 4·7; N, 3·9%).

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