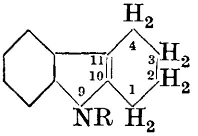
CCCCLXI.—*The Action of Halogens on Polycyclic Indole Derivatives. Part I. The Reaction between Bromine and the Acyl Derivatives of Tetrahydrocarbazole and Benzopentindole.*

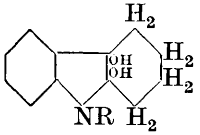
By SYDNEY GLENN PRESTON PLANT and MURIEL LOUISE TOMLINSON.

IN a previous series of papers (for references, see footnote, this vol., p. 93; also this vol., pp. 1990, 2218) it has been shown that nitric acid reacts with the acyl derivatives of various polycyclic indoles to give not only simple nitro-compounds but also substances which have been formed by the addition of either OH and NO_2 or 2OH at the 2 : 3-positions in the indole skeleton. In view of the interest attaching to the ability of these indole derivatives to form such addition complexes and of the remarkable transformations which the products have been found to undergo, it became of importance to study the behaviour of some of these acyl compounds towards other reagents. The present communication describes primarily the results obtained during an examination of the action of bromine upon certain acyl derivatives of tetrahydrocarbazole and benzopentindole.

When 9-acetyltetrahydrocarbazole (I; R = Ac) was treated with an equimolecular proportion of bromine in acetic acid solution, the product, which was isolated by immediate dilution with water, was found to contain only a negligible amount (0·2%) of bromine, so that the reaction which had taken place gave no appreciable quantity of a simple substitution product. An investigation of this material indicated that it consisted essentially of 10 : 11-dihydroxy-9-acetylhexahydrocarbazole (II; R = Ac), which was one of the substances obtained by Perkin and Plant (J., 1923, **123**, 676) from the action of nitric acid upon 9-acetyltetrahydrocarbazole. A further study of the reaction showed that this substance had resulted from the primary addition of bromine at the 10 : 11-positions and the subsequent hydrolysis of the dibromide (III) when the reaction mixture was poured into water. Thus, when the bromination was carried out in carbon disulphide, the dibromide (III) was precipitated as an extremely unstable solid which rapidly evolved hydrogen bromide and immediately gave (II; R = Ac) on treatment with water. It is clear from the results described below that the spontaneous elimination of hydrogen bromide from the dibromide (III) involves dehydrogenation at the 1- and 4-positions, but attempts to isolate the products under anhydrous conditions have not proved successful.



(I.)



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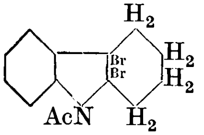
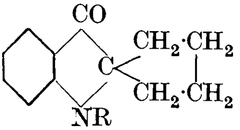


(III.)

When 9-benzoyltetrahydrocarbazole (I; R = Bz) was brominated under similar conditions, a product, $C_{19}H_{17}O_2N$, was isolated from the sticky solid obtained by pouring the reaction mixture into water. It is obvious that this compound is not 10 : 11-dihydroxy-9-benzoylhexahydrocarbazole (II; R = Bz), a substance already described by Plant and Rutherford (J., 1929, 1974), and differs from the latter in containing one molecule of water less. Owing to the fact that the substance (II; R = Ac) can be made to lose a molecule of water under certain conditions to yield 6-acetyl-ψ-indoxyl*spirocyclo*pentane (IV; R = Ac), it was thought that this new product might be the corresponding benzoyl compound (IV; R = Bz). This possibility was, however, eliminated by the preparation of the latter *compound* by the direct benzoylation of ψ-indoxyl*spirocyclo*pentane (IV; R = H). It is extremely probable, therefore, that the product $C_{19}H_{17}O_2N$ has resulted from the primary addition of two bromine atoms, followed by the elimination of one molecule of hydrogen bromide and the replacement of the remaining bromine by hydroxyl.



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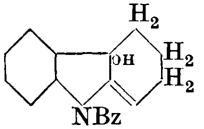

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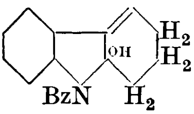
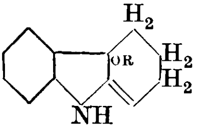


(VI.)

There are two possible formulæ (V and VI) for this compound, and, of these, we consider (V) to be the more probable, since the bromine atom in the 10-position is likely to be the more readily removed, and the substance has been called 11-*hydroxy*-9-*benzoyl*-2 : 3 : 4 : 11-*tetrahydrocarbazole*. When the compound was hydrolysed by alcoholic alkali, the benzoyl group was removed with the formation of 11-*hydroxy*-2 : 3 : 4 : 11-*tetrahydrocarbazole* (VII; R = H), but, when the latter was then treated with benzoyl chloride and alkali in acetone solution, only one benzoyl group was introduced, and the product, which was not identical with (V), was apparently 11-*benzoyloxy*-2 : 3 : 4 : 11-*tetrahydrocarbazole* (VII; R = Bz).

When the compound (V) was boiled in acetic anhydride for several hours and the product was distilled under reduced pressure, a small quantity of a substance, $C_{19}H_{11}ON$, was obtained. It is suggested that this is 19-*ketophenanthridindocoline* * (VIII), and experiments are being carried out with a view to confirming this. It is clear that its formation has resulted from combined dehydration and dehydrogenation, but it is not possible at present to be certain of the mechanism of the process or to state whether it proceeds



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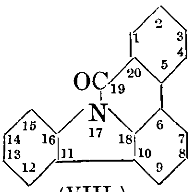
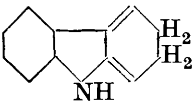


(VIII.)



(IX.)

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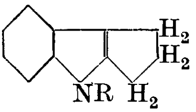
* At the suggestion of the Editor the name "phenanthridindocoline" has been adopted for the parent compound (VIII, with H_2 in place of O).

entirely during the treatment with acetic anhydride or partly during the subsequent distillation. It was found that the substance (V) gave carbazole on distillation under reduced pressure. When 11-hydroxy-2 : 3 : 4 : 11-tetrahydrocarbazole was boiled with acetic anhydride for an hour, a molecule of water was removed with the formation of 2 : 3-*dihydrocarbazole* (IX).

Treatment of ethyl tetrahydrocarbazole-9-carboxylate (I; R = CO_2Et) with bromine under similar conditions has not led to the isolation of a pure reaction product. 9-Phenylacetyltetrahydrocarbazole (I; R = $CH_2Ph{\cdot}CO$), on bromination in acetic acid and subsequent addition of water, yielded a product from which a small amount of 10 : 11-dihydroxy-9-phenylacetylhexahydrocarbazole (II; R = $CH_2Ph{\cdot}CO$) was isolated. This substance was found to be identical with one of the compounds obtained by Perkin and Plant (*loc. cit.*) from the action of nitric acid on 9-phenylacetyltetrahydrocarbazole. Finally it was shown that the bromination product of 9-cinnamoyltetrahydrocarbazole (I; R = $CHPh{:}CH{\cdot}CO$) yielded, after treatment with water, a solid (A) from which 11-*hydroxy*-9-*cinnamoyl*-2 : 3 : 4 : 11-*tetrahydrocarbazole* (analogous to V) was obtained. Hydrolysis of the latter gave 11-hydroxy-2 : 3 : 4 :11-tetrahydrocarbazole (VII; R = H). The crude solid (A) was distilled under reduced pressure, and both cinnamic acid and carbazole were extracted from the distillate.

The results described above serve definitely to establish that the interaction of the 9-acyltetrahydrocarbazoles and an equimolecular quantity of bromine involves no appreciable substitution. The 10 : 11-dibromides, moreover, are extremely unstable and may readily lose hydrogen bromide. Furthermore, both the bromine atoms are very readily replaced by hydroxyl groups by the action of water. The formation of compounds of the type (V) undoubtedly involves the loss of a molecule of hydrogen bromide from the primary addition product; they are not derived by the loss of water from the dihydroxy-compounds (II), since the latter are known to be stable under the experimental conditions employed, and, when they lose water under more vigorous treatment, they yield the *spiro*-compounds (IV).

Since the 8-acyldihydropentindoles (X) differ greatly from the closely related 9-acyltetrahydrocarbazoles in their additive reactions with nitric acid, it was decided to examine the behaviour of some of the former towards bromine. The acetyl, benzoyl, carbethoxy, and *phenylacetyl* derivatives were employed, but in every case intense colours were developed on bromination in acetic acid solution, and all efforts to isolate definite reaction products have failed. Similar results were obtained with dihydropentindole itself. With tetrahydropentindole (XI) and its 8-acetyl derivative, in which the reactive double linkage is no longer present, it is to be expected that



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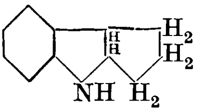
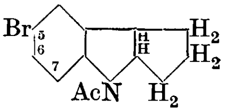


(XI.)



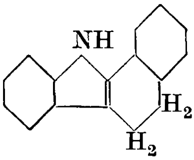
(XII.)

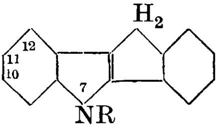
these phenomena would not be realised. This has been shown to be the case, and both, on bromination, undergo substitution in the normal positions. Thus 8-acetyltetrahydropentindole, with an equimolecular proportion of bromine in acetic acid solution, gave exclusively 5-*bromo*-8-*acetyltetrahydropentindole* (XII), the constitution of which was established by its synthesis by the reduction and subsequent acetylation of 5-*bromodihydropentindole*, which, in turn, was obtained by an application of the Fischer indole synthesis to *cyclo*pentanone-*p*-bromophenylhydrazone. Tetrahydropentindole itself underwent substitution so readily that, even when a unimolecular proportion of bromine was used, considerable quantities of a dibromo-compound were formed. Thus the product, on acetylation, gave only a small amount of 5-bromo-8-acetyltetrahydropentindole, and a much greater quantity of a derivative which was undoubtedly 5 : 7-*dibromo*-8-*acetyltetrahydropentindole*.

The earlier work referred to in the opening sentence has shown that addition compounds of the types produced when nitric acid acts upon the 9-acyltetrahydrocarbazoles and the 8-acyldihydropentindoles are far more difficult to obtain from analogous, but more complex, polycyclic indoles. In view of this it became of interest to extend the present investigation to the bromination of the acyl derivatives of 5 : 6-dihydro-αβ-naphthacarbazole (XIII) and of benzopentindole (XIV; R = H). Unfortunately, previous efforts (Bryant and Plant, this vol., p. 93) to prepare the 11-acyl-5 : 6-dihydro-αβ-naphthacarbazoles have been unsuccessful, so that these experiments have, of necessity, been limited to derivatives of (XIV).

When bromine and 7-acetylbenzopentindole (XIV; R = Ac) were made to react in acetic acid solution, the product was separable into

(XIII.)





(XIV.)

two substances, m. p.'s 150° and 168°, which were found, on analysis, to be simple monobromo-7-acetylbenzopentindoles. In order to establish the structures of these compounds, Fischer's indole synthesis was applied to the *m*- and *p*-bromophenylhydrazones of α-hydrindone; attempts to apply the same reaction to the *o*-bromo-analogue were unsuccessful. The former of the two hydrazones can theoretically give a mixture of both 10-bromo- and 12-bromo-benzopentindole, and, since fractions obtained from the reaction product melted with decomposition and were unsuitable for definite characterisation, the whole was acetylated. Fractional crystallisation of the product then led to the isolation of both the possible bromo-compounds. Since there is no evidence to show which of these is the 10-bromo- and which the 12-bromo-compound, the procedure previously adopted in analogous cases has been employed, and one (m. p. 150°) has been called 10(or 12)-*bromo*-7-*acetylbenzopentindole* and the other (m. p. 168°) 12(or10)-*bromo*-7-*acetylbenzopentindole*. It was found that these two acetyl compounds were identical with the products obtained from the bromination of 7-acetylbenzopentindole. 11-*Bromo*-7-*acetylbenzopentindole*, derived from the *p*-bromophenylhydrazone by an analogous procedure, melted at 174° and was definitely not identical with either bromination product.

From the product of the action of bromine under similar conditions on 7-benzoylbenzopentindole (XIV; R = Bz) a single monobromo-derivative has been isolated, and this was identified as 10(or 12)-*bromo*-7-*benzoylbenzopentindole* by hydrolysis and subsequent acetylation. The bromination of *ethyl benzopentindole*-7-*carboxylate* (XIV; R = CO_2Et) has given a mixture of *ethyl* 10(or 12)-*bromobenzopentindole*-7-*carboxylate* and the isomeric 12(or 10)-*bromo*-compound. The constitution of the former was again established by hydrolysis and subsequent acetylation, while the structure of the latter was determined by its synthesis from 12(or 10)-bromo-7-acetylbenzopentindole, which was hydrolysed and then treated with alkali and ethyl chloroformate in acetone solution. In no case was it possible to isolate any addition product or a substance derived from such a product by reactions analogous to those described in the earlier part of this paper.

In view of the fact that addition at the double linkage takes place so readily when bromine reacts with the 9-acyltetrahydrocarbazoles, it is surprising that only substitution products have been isolated from the bromination of the closely related 7-acylbenzopentindoles. The tendency to form addition complexes is apparently diminished to a remarkable extent by the presence of an additional benzene nucleus in the molecule of the polycyclic indole. In all the bromo-compounds now described the bromine atom has entered a position in the benzene nucleus which is meta with respect to the $>$ NR group. The earlier work on the nitration of the acylated polycyclic indoles has shown that these are the positions always taken by the nitro-group during substitution in this series.

EXPERIMENTAL.

Bromination of 9-*Acetyltetrahydrocarbazole.*—(a) Bromine (6 g.), dissolved in acetic acid, was added gradually, with stirring and at room temperature, to a solution of 9-acetyltetrahydrocarbazole (8 g.) in glacial acetic acid, and the whole was then immediately poured into water. When the pale yellow precipitate was twice recrystallised from alcohol, 10 : 11-dihydroxy-9-acetylhexahydrocarbazole was isolated in colourless plates, m. p. 203° (Found : C, 68·1 ; H, 6·8. Calc. : C, 68·0 ; H, 6·9%), unchanged by admixture with the compound as made by Perkin and Plant (*loc. cit.*).

(b) When bromine (1·5 g.) was added to a solution of 9-acetyltetrahydrocarbazole (2 g.) in a little dry carbon disulphide, a bright yellow precipitate (m. p. 60° decomp.) immediately appeared. Since this rapidly evolved hydrogen bromide and could not in consequence be purified by recrystallisation, water was added to the reaction mixture and the whole was well shaken. The product then changed to a colourless solid, which remained suspended in the aqueous layer and was found, on crystallisation from alcohol, to be 10 : 11-dihydroxy-9-acetylhexahydrocarbazole. The carbon disulphide layer, on evaporation, yielded a yellow oil from which nothing crystalline has been obtained.

Bromination of 9-*Benzoyltetrahydrocarbazole.*—When a solution of 9-benzoyltetrahydrocarbazole (10 g., prepared as described by Perkin and Plant, *loc. cit.*) in glacial acetic acid was treated gradually at room temperature with bromine (5·8 g.), dissolved in acetic acid, the colour darkened and hydrogen bromide was evolved. The reaction mixture was immediately poured into an excess of water, and a sticky solid was obtained. The latter was repeatedly extracted with small quantities of petroleum (b. p. 60—80°) ; a colourless substance separated from the solvent on cooling, and, after further recrystallisation from the same solvent, 11-*hydroxy*-9-*benzoyl*-2 : 3 : 4 : 11-*tetrahydrocarbazole* was ultimately isolated in colourless prisms, m. p. 144—146° (Found : C, 78·5 ; H, 5·7. $C_{19}H_{17}O_2N$ requires C, 78·4 ; H, 5·8%). When the substance was admixed with 10 : 11-dihydroxy-9-benzoylhexahydrocarbazole (m. p. 142°), prepared as described by Plant and Rutherford (*loc. cit.*), the m. p. was depressed to 120°. The dilute acetic acid mother-liquor gradually deposited a considerable quantity of a yellow solid, which was sparingly soluble in most solvents and has not been obtained crystalline. When, however, the mother-liquor was immediately made alkaline by the addition of ammonia and ice, a colourless solid slowly separated, and this, on recrystallisation from petroleum, proved to be a further quantity of 11-hydroxy-9-benzoyl-2 : 3 : 4 : 11 tetrahydrocarbazole. The total yield of the latter product, which was much improved by the addition of charcoal during the extraction process, amounted to 4·9 g. The substance gave carbazole (identified by mixed m. p.) when distilled under reduced pressure and then crystallised successively from methyl alcohol and toluene.

11-*Hydroxy*-2 : 3 : 4 : 11-*tetrahydrocarbazole*.—When a mixture of 11-hydroxy-9-benzoyl-2 : 3 : 4 : 11-tetrahydrocarbazole (1 g.), potassium hydroxide (4 g.), water (8 c.c.), and alcohol (25 c.c.) was boiled for 15 minutes and then diluted with water, 11-*hydroxy*-2 : 3 : 4 : 11-*tetrahydrocarbazole* was precipitated. After recrystallisation from benzene, it was obtained in colourless prisms, m. p. 115° (Found : C, 77·1; H, 6·9. $C_{12}H_{13}ON$ requires C, 77·0; H, 6·9%).

The latter product (1 g.) was dissolved in a mixture of a little acetone and aqueous potassium hydroxide (6 g. of 66%) and treated with benzoyl chloride (2 c.c.) with vigorous shaking. When the product, which was isolated by dilution with water, was crystallised from petroleum (b. p. 60—80°) (charcoal), 11-*benzoyloxy*-2 : 3 : 4 : 11-*tetrahydrocarbazole* was obtained in colourless prisms, m. p. 128° (Found : C, 78·4; H, 6·0; N, 5·1. $C_{19}H_{17}O_2N$ requires C, 78·4; H, 5·8; N, 4·8%). The m. p. was depressed by admixture with the compound (m. p. 144—146°) derived from the bromination of 9-benzoyltetrahydrocarbazole.

When a solution of 11-hydroxy-2 : 3 : 4 : 11-tetrahydrocarbazole in acetic anhydride was boiled for an hour and then cooled, 2 : 3-*dihydrocarbazole* separated. After recrystallisation from benzene, it was obtained in colourless prisms, m. p. 293—295° (Found : C, 85·1; H, 6·5. $C_{12}H_{11}N$ requires C, 85·2; H, 6·5%).

19-*Ketophenanthridindocoline*.—A solution of 11-hydroxy-9-benzoyl-2 : 3 : 4 : 11-tetrahydrocarbazole (5 g.) in acetic anhydride (40 c.c.) was boiled under reflux for 9½ hours and then shaken with an excess of water. Since the solid product could not be crystallised, it was distilled under reduced pressure, and a substance, b. p. about 300°/16 mm., was collected. When the latter had been crystallised several times from alcohol, 19-*ketophenanthridindocoline* was obtained in yellow needles, m. p. 225° (Found : C, 84·6; H, 4·3; N, 5·2. $C_{19}H_{11}ON$ requires C, 84·7; H, 4·1; N, 5·2%).

6-*Benzoyl*-ψ-*indoxyl*spirocyclo*pentane*.—Benzoyl chloride (2 c.c.) was added with vigorous shaking to a mixture of ψ-indoxyl*spiro*-*cyclo*pentane (1 g.) and aqueous potassium hydroxide (4·5 g. of 66%) in a little acetone. After dilution with water, the oily product soon solidified, and, on crystallisation from alcohol, 6-*benzoyl*-ψ-*indoxyl*-

spirocyclo*pentane* was obtained in colourless prisms, m. p. 107° (Found : N, 5·1. $C_{19}H_{17}O_2N$ requires N, 4·8%).

Bromination of 9-*Phenylacetyltetrahydrocarbazole.*—Bromine (5·4 g.), dissolved in acetic acid, was added gradually to a solution of 9-phenylacetyltetrahydrocarbazole (10 g., prepared as described by Perkin and Plant, *loc. cit.*) in glacial acetic acid. Hydrogen bromide was evolved, and, when the mixture was poured into much water and the resulting solid was crystallised successively from benzene–petroleum and alcohol, a small quantity of 10 : 11-dihydroxy-9-phenylacetylhexahydrocarbazole was obtained in colourless prisms, m. p. 169°, unchanged by admixture with the compound as made by Perkin and Plant (*loc. cit.*).

Bromination of 9-*Cinnamoyltetrahydrocarbazole.*—The following method for the preparation of 9-cinnamoyltetrahydrocarbazole was found to be preferable to that described by Plant and Rutherford (*loc. cit.*). A solution of ethyl bromide (4·7 g.) in dry ether (100 c.c.) was treated with magnesium (0·8 g.), and, after the reaction was completed, tetrahydrocarbazole (5·8 g.) was added gradually. When the mixture had been warmed for a few minutes, it was treated with a dry ethereal solution of cinnamoyl chloride (6 g.), with shaking, and, after an hour, dilute hydrochloric acid was added. The ethereal solution was washed with aqueous sodium carbonate, dried, and evaporated. The residue solidified on treatment with alcohol, and, after crystallisation from this solvent, 9-cinnamoyltetrahydrocarbazole was obtained in yellow needles, m. p. 117°.

When bromine (2·65 g.), dissolved in acetic acid, was added gradually to a solution of 9-cinnamoyltetrahydrocarbazole (5 g.) in glacial acetic acid, the mixture became green and evolved hydrogen bromide. On its being poured into water, a yellow solid was precipitated. The latter was collected, washed with dilute aqueous ammonia, and purified by boiling its solution in petroleum (b. p. 60—80°) for ½ hour with the addition of a considerable quantity of charcoal. A crystalline product slowly separated from the filtered solution on cooling, and, after further recrystallisation first from petroleum and then from methyl alcohol, 11-*hydroxy*-9-*cinnamoyl*-2 : 3 : 4 : 11-*tetrahydrocarbazole* was isolated in yellow prisms, m. p. 102—106° (Found : C, 79·4 ; H, 6·0. $C_{21}H_{19}O_2N$ requires C, 79·5 ; H, 6·0%).

When either the latter substance or the crude bromination product was boiled for an hour in aqueous-alcoholic potassium hydroxide and the mixture was poured into a little water, a solid separated, on cooling, and this, after recrystallisation from benzene, was obtained in colourless prisms, m. p. 115°. It was shown by a mixed m. p. to be 11-hydroxy-2 : 3 : 4 : 11-tetrahydrocarbazole, identical with the product described earlier in this paper. Acidification of the alkaline mother-liquor resulted in the precipitation of cinnamic acid.

The crude product of the bromination of 9-cinnamoyltetrahydrocarbazole was distilled under reduced pressure. The semi-solid distillate was first extracted with hot water, from which, after filtration and cooling, cinnamic acid separated. The residue was then crystallised from toluene, and carbazole (m. p. 238°) was obtained.

8-*Phenylacetyldihydropentindole.*—Prepared by a process essentially similar to that described for 9-cinnamoyltetrahydrocarbazole, this substance proved to be only sparingly soluble in ether. Consequently it was collected by filtration after the ultimate reaction mixture had been treated with dilute hydrochloric acid, and crystallised from alcohol, from which it separated in colourless needles, m. p. 116° (Found : N, 5·0. $C_{19}H_{17}ON$ requires N, 5·1%).

Bromination of 8-*Acetyltetrahydropentindole.*—When bromine (2·4 g.), dissolved in acetic acid, was added slowly at room temperature to a solution of 8-acetyltetrahydropentindole (3 g., prepared as described by Plant and Rippon, J., 1928, 1911) in glacial acetic acid, the product separated as an oil which rapidly solidified. Since this was largely in the form of a hydrobromide, it was treated with alkali, and then crystallised from alcohol, from which 5-*bromo*-8-*acetyltetrahydropentindole* separated in colourless needles, m. p. 114° (Found : N, 5·1. $C_{13}H_{14}ONBr$ requires N, 5·0%).

*cyclo*Pentanone-*p*-bromophenylhydrazone was readily formed as a solid when the corresponding hydrazine (5·5 g.) and *cyclo*pentanone (2·3 g.) were mixed. On recrystallisation of a sample from alcohol, it was isolated in colourless plates, m. p. 109°, but it soon decomposed on keeping. A mixture of the crude hydrazone, water (180 c.c.), and concentrated sulphuric acid (20 c.c.) was boiled for 10 minutes, and, after the solution had been cooled and diluted, 5-*bromodihydropentindole* appeared as a solid, which, on crystallisation from petroleum, was obtained in colourless needles, m. p. 140° (Found : N, 5·8. $C_{11}H_{10}NBr$ requires N, 5·9%). A solution of this indole (5 g.) in sulphuric acid (200 c.c. of 60%) was submitted to reduction in the cathode compartment of an electrolytic cell at 100°, lead electrodes being used and a current of 5 amps. (approximately 0·025 amp. per sq. cm. of cathode) for 7 hours. After the mixture had been made alkaline with aqueous ammonia (*d* 0·880), the temperature being kept low, the product was extracted with ether, and the ethereal solution was dried with potassium carbonate and evaporated. The residue then solidified, and, after recrystallisation from alcohol, 5-*bromotetrahydropentindole* was obtained in red prisms, m. p. 73°

(Found : C, 55·7 ; H, 5·0. $C_{11}H_{12}NBr$ requires C, 55·5 ; H, 5·0%). When a solution of the latter substance (2 g.) in acetic anhydride (20 c.c.) was boiled for ½ hour and then well shaken with water, a product was obtained which, after recrystallisation from alcohol, yielded 5-bromo-8-acetyltetrahydropentindole in colourless needles, m. p. 114°, identical with the compound described above.

Bromination of Tetrahydropentindole.—A solution of tetrahydropentindole (3 g., prepared by the method of Plant and Rippon, *loc. cit.*) in glacial acetic acid was treated with bromine (3·0 g.), also dissolved in acetic acid, and the mixture was then made alkaline by the addition of dilute aqueous ammonia. The oily product was extracted in ether, recovered from the dried solution, and acetylated by boiling for 2 hours with acetic anhydride. After the resulting solution had been shaken with water, a solid gradually separated, and, on crystallisation from alcohol, it became obvious that it was a mixture of two substances. These were separated by fractional crystallisation from alcohol, and one (m. p. 107°), which was present in small quantity only, was shown by a mixed m. p. to be nearly pure 5-bromo-8-acetyltetrahydropentindole. The main constituent of the mixture, which was 5 : 7-*dibromo*-8-*acetyltetrahydropentindole*, separated from alcohol in colourless prisms, m. p. 145° (Found : C, 43·3 ; H, 3·6. $C_{13}H_{13}ONBr_2$ requires C, 43·5 ; H, 3·6%).

11-*Bromo*-7-*acetylbenzopentindole.*—*p*-Bromophenylhydrazine (5·2 g.) and α-hydrindone (4·73 g.) were melted together on the steam-bath and stirred until solidification took place. When a small specimen was crystallised from alcohol, α-hydrindone-*p*-bromophenylhydrazone was obtained in colourless needles which melted rather indefinitely at 153—159° owing to slight decomposition. The crude hydrazone was boiled with dilute sulphuric acid (27%) for 10 minutes and the mixture was diluted with water. After the product had been crystallised from alcohol, 11-*bromobenzopentindole* was obtained in colourless plates, m. p. 230° (Found : C, 63·8 ; H, 3·8. $C_{15}H_{10}NBr$ requires C, 63·4 ; H, 3·5%). A solution of the latter (1 g.) in acetone (25 c.c.) and aqueous sodium hydroxide (5 g. of 50%) was treated gradually with acetyl chloride (3·5 c.c.), the whole being well shaken. After the product had been isolated by dilution with water and crystallised from alcohol, 11-*bromo*-7-*acetylbenzopentindole* was obtained in yellow needles, m. p. 174° (Found : C, 62·3 ; H, 3·8. $C_{17}H_{12}ONBr$ requires C, 62·6 ; H, 3·7%). When its solution in aqueous-alcoholic potassium hydroxide had been boiled for ½ hour and then diluted with water, 11-bromobenzopentindole was precipitated in a pure condition.

10(or 12)-*Bromo- and* 12(or 10)-*Bromo*-7-*acetylbenzopentindole.*—After a mixture of molecular proportions of *m*-bromophenylhydrazine and α-hydrindone had been heated for 10 minutes on a steam-bath, the hydrazone solidified, on cooling, and separated from alcohol in colourless needles, m. p. 118—120°. It was then boiled for 20 minutes with dilute sulphuric acid (27%), and the mixture of crude indoles, which was collected after dilution with water, was acetylated by a procedure similar to that described above for 11-bromo-7-acetylbenzopentindole. When the product was recrystallised twice from alcohol and then from acetic acid, 10(or 12)-*bromo*-7-*acetylbenzopentindole* was obtained in pale yellow needles, m. p. 150° (Found: C, 62·7; H, 3·8%). After the first alcoholic mother-liquor had been completely evaporated and the residue recrystallised successively from acetone and alcohol, 12(or 10)-*bromo*-7-*acetylbenzopentindole* was isolated in pale yellow needles, m. p. 168° (Found: C, 62·8; H, 3·8%). The amounts of the 10(or 12)-bromo- and the 12(or 10)-bromo-compounds were in the ratio of approximately 5 : 1.

*α-Hydrindone-*o*-bromophenylhydrazone.*—This hydrazone was prepared by heating the corresponding ketone (5·7 g.) with *o*-bromophenylhydrazine (8 g.) for 10 minutes on the steam-bath, and, after cooling and crystallisation from alcohol, it yielded a mixture of colourless needles, m. p. 136°, and red prisms, m. p. 134° (Found: C, 59·8; H, 4·3. $C_{15}H_{13}N_2Br$ requires C, 59·8; H, 4·3%). The authors are indebted to Dr. F. D. Chattaway, who has examined these two forms and expressed the view that they are polymorphic modifications of the hydrazone. The colourless needles slowly change into the red prisms on long standing in contact with alcohol. All attempts to convert this hydrazone into the corresponding 9-bromobenzopentindole have been unsuccessful.

Bromination of 7-*Acetylbenzopentindole.*—A solution of bromine (5·1 g.) in acetic acid (50 c.c.) was added gradually at room temperature, with stirring, to 7-acetylbenzopentindole (8 g., prepared as described by Leuchs and Kowalski, *Ber.*, 1925, **58**, 2825), dissolved in a relatively large volume of glacial acetic acid. The solution was then poured into water, and, after the precipitate had been recrystallised several times from alcohol and acetone, 10(or 12)-bromo-7-acetylbenzopentindole (m. p. 150°) was obtained. The m. p. was not depressed by admixture with the synthetical compound described above. When the earlier mother-liquors from the purification of this product were evaporated, a sticky residue was left, but this, on standing for several days with acetone, deposited yellow needles. After being twice recrystallised from alcohol, the latter melted at 168°, and were shown by a mixed m. p. to be identical with the synthetical 12(or 10)-bromo-7-acetylbenzopentindole. The amounts of the 10(or 12)-bromo- and the 12(or 10)-bromo-compounds formed in this reaction were in the ratio of approximately 5 : 1.

Bromination of 7-Benzoylbenzopentindole.—The product of the interaction of bromine (6 g.) and 7-benzoylbenzopentindole (8 g., prepared as described by Bryant and Plant, *loc. cit.*) in acetic acid solution was precipitated on pouring into water. After being twice recrystallised from alcohol and then from acetic acid, 10(or 12)-*bromo-7-benzoylbenzopentindole* was obtained in colourless needles, m. p. 193° (Found : C, 68·2 ; H, 3·7. $C_{22}H_{14}ONBr$ requires C, 68·0 ; H, 3·6%). A solution of the latter (2 g.) in aqueous-alcoholic potassium hydroxide was boiled for ½ hour, and the product, which was isolated by pouring into water, was dissolved in acetone containing aqueous potassium hydroxide (10 g. of 50%), and shaken with acetyl chloride (7 c.c.). When the resulting mixture was diluted with water and the precipitate crystallised from alcohol, 10(or 12)-bromo-7-acetylbenzopentindole, identical with a synthetical specimen, was obtained.

Bromination of Ethyl Benzopentindole-7-carboxylate.—A solution of benzopentindole (6 g.) in acetone containing aqueous potassium hydroxide (16·5 g. of 66%) was treated gradually with ethyl chloroformate (9 g.), with vigorous shaking, and the product was precipitated by dilution with water. After crystallisation from alcohol, *ethyl benzopentindole-7-carboxylate* was obtained in colourless needles, m. p. 116° (Found : N, 5·1. $C_{18}H_{15}O_2N$ requires N, 5·1%).

A solution of the latter (8 g.) in acetic acid was treated gradually with bromine (4·6 g.), dissolved in acetic acid, and the mixture was poured into water. After being twice recrystallised from alcohol, *ethyl* 10(or 12)-*bromobenzopentindole-7-carboxylate* (5 g.) was obtained in colourless needles, m. p. 166° (Found : C, 60·5 ; H, 3·9. $C_{18}H_{14}O_2NBr$ requires C, 60·7 ; H, 3·9%). When the alcoholic mother-liquors were evaporated and the sticky residue left in contact with acetone, a solid separated. This was treated with a little hot alcohol to extract any of the more soluble 10(or 12)-bromo-compound described above. The remainder was then twice recrystallised from a larger volume of alcohol, and *ethyl* 12(or 10)-*bromobenzopentindole-7-carboxylate* (1 g.) was isolated in colourless needles, m. p. 127° (Found : C, 60·5 ; H, 4·1%). The latter compound was synthesised by boiling a solution of 12(or 10)-bromo-7-acetylbenzopentindole in aqueous-alcoholic potassium hydroxide for ½ hour and treating the product in acetone solution with concentrated aqueous alkali and ethyl chloroformate. The m. p. of a mixture of the synthetical compound and the direct bromination product showed no depression.

When ethyl 10(or 12)-bromobenzopentindole-7-carboxylate was boiled in aqueous-alcoholic potassium hydroxide for ½ hour and the product was treated in acetone solution with alkali and acetyl chloride, 10(or 12)-bromo-7-acetylbenzopentindole (m. p. 150°, after crystallisation from alcohol), identical with a synthetical specimen, was obtained.

THE DYSON PERRINS LABORATORY,
OXFORD.

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